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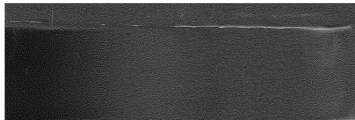

(54) **ZINC OR ZINC ALLOY ELECTROPLATING METHOD AND SYSTEM**

(57) The present invention provides a zinc or zinc alloy electroplating method comprising: performing energizing in an alkaline zinc or zinc alloy electroplating bath provided with a cathode and an anode, wherein the anode is an anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics, the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc plating bath containing an organic compound additive or an alkaline zinc alloy electroplating

bath containing an amine chelating agent or an organic compound additive, oxidation decomposition, on a surface of the anode caused by the energizing, of the organic compound additive in the alkaline zinc plating bath or the amine chelating agent and the organic compound additive in the alkaline zinc alloy electroplating bath is suppressed as compared with a case of using as an anode the same conductive substrate uncoated with the alkali-resistant ceramics.

FIG.1

EXAMPLE 1

ENERGIZING QUANTITY	DISTANCE FROM LEFT END OF HULL CELL (cm)	1	2	3	5	7	9	11	13	15	17	19
0 Ah/L	FILM THICKNESS (μm)	17.1	13.1	10.7	7.4	5.3	3.1	1.9	1.1	0.7	0.4	0.2
	Ni (%)	15.7	15.6	15.6	15.6	15.4	15.5	15.5	15.6	14.9	14.5	15.2
	HULL CELL APPEARANCE											
500 Ah/L	FILM THICKNESS (μm)	17.3	13.0	10.4	7.3	5.6	3.5	2.1	1.1	0.7	0.5	0.2
	Ni (%)	15.4	15.4	15.5	15.7	15.6	15.8	15.7	15.5	14.8	14.5	14.7
	HULL CELL APPEARANCE											

Description

Technical Field

[0001] The present invention relates to a zinc or zinc alloy electroplating method and system, and in particular to an electroplating method and system for applying zinc or zinc alloy electroplating excellent in corrosion resistance to a steel member or the like by using an alkaline zinc or zinc alloy electroplating bath, in which the use of an anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics enables long-term use of the electroplating bath while maintaining plating bath performance.

Background Art

[0002] Zinc plating has been used as inexpensive rust-inhibitory plating which uses a cyan compound-containing bath and contains almost no organic compound. However, studies have been made in recent years on a zinc plating bath which uses no highly toxic cyan compound, and zinc plating baths containing organic compounds such as quaternary amine polymers have been prevailing. It is to be noted that the decomposition and disappearance of these organic compounds by anodic oxidation result in dendrite deposition with poor adhesion, making it impossible to carry out good zinc rust-inhibitory plating.

[0003] Zinc alloy plating has corrosion resistance superior to that of zinc plating and thus is widely used for automotive components and the like. In particular, alkaline zinc nickel alloy plating baths are used for fuel parts requiring high corrosion resistance and engine parts placed in a high temperature environment. An alkaline zinc nickel alloy plating bath is a plating bath in which an amine chelating agent suitable for a Ni co-deposition ratio is selected to dissolve nickel, and zinc and nickel are co-deposited as a plating film. However, electroplating by use of an alkaline zinc nickel alloy plating bath encounters a problem of oxidation decomposition of the amine chelating agent on the anode surface during the energizing. In the coexistence of nickel ions and ferrous metal ions such as iron ions, they act as oxidation catalysts to further promote the oxidation decomposition of the amine chelating agent. Therefore, when the alkaline zinc nickel alloy plating bath comes into contact with the anode, the amine chelating agent rapidly decomposes, which rapidly decreases the plating performance. The accumulation of decomposed products causes a number of problems such as decrease in electric current efficiency, increase in bath voltage, decrease in plating film thickness, decrease in nickel content in the plating film, reduction in current density range in which plating is possible, reduction in gloss, and increase in COD. Therefore, it is impossible to use a plating bath for a long time, requiring the replacement of the plating bath.

[0004] Several methods have been so far known as remedies against the above. For example, Published Japanese Translation of PCT International Application No. 2002-521572 discloses a method in which an alkaline zinc nickel alloy plating bath (catholyte) and an acidic anolyte are separated with a positive ion exchange membrane composed of perfluoropolymer. However, in the case of using an acidic solution as the anolyte, an expensive corrosion-resistant member such as platinum-plated titanium has to be used as the anode. In addition, when the separating membrane is broken, an accident may occur in which the acidic solution on the anode side and the alkaline solution on the cathode side mix to cause a sudden chemical reaction. On the other hand, in the case of using an alkaline liquid as the anolyte in place of an acidic liquid, the present inventors conducted a plating test and revealed that the anolyte rapidly transferred to the catholyte due to energizing, causing lowering of the liquid surface level of the anolyte and rising of the liquid surface level of the catholyte at the same time.

[0005] As a method of solving the problems above, Japanese Patent Application Publication No. 2007-2274 describes a method of replenishing an alkaline component to the alkaline anolyte by using a cation exchange membrane. However, this method requires additional equipment, liquid management, and the like, making the operations complicated.

[0006] In addition, International Publication No. WO2016/075963 describes a method of zinc alloy electroplating, including separating the cathode region including the cathode and the anode region including the anode with a negative ion exchange membrane, using an alkaline zinc alloy plating solution as the catholyte included in the cathode region, and using an alkaline aqueous solution as the anolyte included in the anode region. This method suppresses the oxidation decomposition of the amine chelating agent on the anode in the bath but has a problem that negative ions transfer from the plating solution to the anode electrolyte, and sodium carbonate, sodium sulfate, and sodium oxalate rapidly increase and are deposited and precipitated on the film to destroy the film. To prevent this, it is necessary to control the concentration of impurities in the anolyte and to renew the anolyte frequently. In addition, the introduction of an anode cell is not economical because it requires a very expensive facility investment, a large installation site for an anolyte circulation tank, piping, and others, maintenance of the anode cell, regular membrane replacement, and so forth.

[0007] Moreover, Published Japanese Translation of PCT International Application No. 2008-539329 discloses a zinc alloy plating bath in which a cathode and an anode are separated with a filtration membrane. However, the present inventors examined it and revealed that the disclosed filtration membrane was not able to prevent the transfer of the catholyte and the anolyte and was not able to prevent the decomposition of the chelating agent on the anode. In addition,

since the zinc alloy plating solution is also used as the anolyte, the decomposition of the anolyte is greatly promoted, which thus requires replacement of the anolyte. Without the replacement, the decomposed products transfer into the plating solution of the cathode. Therefore, the liquid lifetime was found not to be extended substantially.

5 Summary of Invention

[0008] An object of the present invention is to provide an inexpensive and economical plating method capable of achieving lifetime extension of a zinc or zinc alloy plating bath while maintaining the performance thereof, the method suppressing the oxidation decomposition of a chelating agent or a brightening agent on the anode surface without using a special apparatus such as an expensive anode cell.

[0009] The present invention has been made based on the knowledge that use of an anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics maintains the plating bath performance because oxidation decomposition of the amine chelating agent does not take place on the anode surface in the bath. Specifically, the present invention provides a zinc or zinc alloy electroplating method and system described below.

[1] A zinc or zinc alloy electroplating method comprising:

performing energizing in an alkaline zinc or zinc alloy electroplating bath provided with a cathode and an anode, wherein

the anode is an anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics,

the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc plating bath containing an organic compound additive or an alkaline zinc alloy electroplating bath containing an amine chelating agent or an organic compound additive,

oxidation decomposition, on a surface of the anode caused by the energizing, of the organic compound additive in the alkaline zinc plating bath or the amine chelating agent and the organic compound additive in the alkaline zinc alloy electroplating bath is suppressed as compared with a case of using as an anode the same conductive substrate uncoated with the alkali-resistant ceramics.

[2] The zinc or zinc alloy electroplating method according to [1] described above, wherein the anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics consists of a conductive substrate and an alkali-resistant ceramics coating.

[3] The zinc or zinc alloy electroplating method according to [1] or [2] described above, wherein the conductive substrate contains at least one of nickel and iron.

[4] The zinc or zinc alloy electroplating method according to any one of [1] to [3] described above, wherein the alkali-resistant ceramics contains at least one selected from the group consisting of tantalum oxide, aluminum oxide, tantalum nitride, aluminum nitride, silicon nitride, boron nitride, silicon carbide, and boron carbide.

[5] The zinc or zinc alloy electroplating method according to any one of [1] to [4] described above, wherein the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc electroplating bath at least containing zinc ions, caustic alkali, and an organic compound additive.

[6] The zinc or zinc alloy electroplating method according to any one of [1] to [4] described above, wherein the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc alloy electroplating bath at least containing zinc ions, metal ions, caustic alkali, an amine chelating agent, and an organic compound additive, and the metal ions include at least one selected from the group consisting of nickel ions, iron ions, cobalt ions, tin ions, and manganese ions.

[7] The zinc or zinc alloy electroplating method according to [6] described above, wherein the amine chelating agent contains at least one selected from the group consisting of alkylene amine compounds, alkylene oxide adducts thereof, and alkanolamine compounds.

[8] A zinc or zinc alloy electroplating system comprising:

an alkaline zinc or zinc alloy electroplating bath provided with a cathode and an anode, wherein the anode is an anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics,

the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc plating bath containing an organic compound additive or an alkaline zinc alloy electroplating bath containing an amine chelating agent or an organic compound additive,

oxidation decomposition, on a surface of the anode caused by the energizing, of the organic compound additive in the alkaline zinc plating bath or the amine chelating agent and the organic compound additive in the alkaline

zinc alloy electroplating bath is suppressed as compared with a case of using as an anode the same conductive substrate uncoated with the alkali-resistant ceramics.

[9] The zinc or zinc alloy electroplating system according to [8] described above, wherein

the anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics consists of a conductive substrate and an alkali-resistant ceramics coating.

[10] The zinc or zinc alloy electroplating system according to [8] or [9] described above, wherein the conductive substrate contains at least one of nickel and iron.

[11] The zinc or zinc alloy electroplating method according to any one of [8] to [10] described above, wherein the alkali-resistant ceramics contains at least one selected from the group consisting of tantalum oxide, aluminum oxide, tantalum nitride, aluminum nitride, silicon nitride, boron nitride, silicon carbide, and boron carbide.

[12] The zinc or zinc alloy electroplating method according to any one of [8] to [11] described above, wherein the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc electroplating bath at least containing zinc ions, caustic alkali, and an organic compound additive.

[13] The zinc or zinc alloy electroplating method according to any one of [8] to [11] described above, wherein the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc alloy electroplating bath at least containing zinc ions, metal ions, caustic alkali, an amine chelating agent, and an organic compound additive, and the metal ions include at least one selected from the group consisting of nickel ions, iron ions, cobalt ions, tin ions, and manganese ions.

[14] The zinc or zinc alloy electroplating method according to [13] described above, wherein the amine chelating agent contains at least one selected from the group consisting of alkylene amine compounds, alkylene oxide adducts thereof, and alkanolamine compounds.

[0010] The present invention makes it possible to provide an economical plating method and system capable of achieving lifetime extension while maintaining zinc or zinc alloy electroplating bath performance.

Brief Description of Drawings

[0011]

Fig. 1 illustrates the results (plating appearance) of a plating test in accordance with a hull cell test of Example 1.

Fig. 2 illustrates the results (plating appearance) of a plating test in accordance with a hull cell test of Example 2.

Fig. 3 illustrates the results (plating appearance) of a plating test in accordance with a hull cell test of Example 3.

Fig. 4 illustrates the results (plating appearance) of a plating test in accordance with a hull cell test of Comparative Example 1.

Fig. 5 illustrates the results (plating appearance) of a plating test in accordance with a hull cell test of Comparative Example 2.

Fig. 6 illustrates the results (film thickness distribution) of a plating test in accordance with a hull cell test of Example 1.

Fig. 7 illustrates the results (Ni co-deposition ratio distribution) of a plating test in accordance with a hull cell test of Example 1.

Fig. 8 illustrates the results (film thickness distribution) of a plating test in accordance with a hull cell test of Example 2.

Fig. 9 illustrates the results (Ni co-deposition ratio distribution) of a plating test in accordance with a hull cell test of Example 2.

Fig. 10 illustrates the results (film thickness distribution) of a plating test in accordance with a hull cell test of Example 3.

Fig. 11 illustrates the results (Ni co-deposition ratio distribution) of a plating test in accordance with a hull cell test of Example 3.

Fig. 12 illustrates the results (film thickness distribution) of a plating test in accordance with a hull cell test of Comparative Example 1.

Fig. 13 illustrates the results (Ni co-deposition ratio distribution) of a plating test in accordance with a hull cell test of Comparative Example 1.

Fig. 14 illustrates the results (film thickness distribution) of a plating test in accordance with a hull cell test of Comparative Example 2.

Fig. 15 illustrates the results (Ni co-deposition ratio distribution) of a plating test in accordance with a hull cell test of Comparative Example 2.

Description of Embodiments

[0012] A zinc or zinc alloy electroplating method of the present invention includes performing energizing in an alkaline

zinc alloy electroplating bath provided with a cathode and an anode.

[0013] Examples of the metal combined with zinc as zinc alloy plating include one or more metals selected from nickel, iron, cobalt, tin, and manganese. Specific examples include, but are not limited to, zinc nickel alloy plating, zinc iron alloy plating, zinc cobalt alloy plating, zinc manganese alloy plating, zinc tin alloy plating, and zinc nickel cobalt alloy plating. The zinc alloy plating is preferably zinc nickel alloy plating.

[0014] The cathode is a plateable object to be subjected to zinc or zinc alloy electroplating. Examples of the plateable object include objects of various shapes such as plate-shaped objects, rectangular parallelepipeds, cylinders, hollow cylinders, and spherical objects of various metals including iron, nickel, and copper, alloys thereof, and metals and alloys including aluminum subjected to zinc substitution treatment.

[0015] The anode used is an anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics. Examples of the alkali-resistant ceramics include, but are not limited to, tantalum oxide, aluminum oxide, tantalum nitride, aluminum nitride, silicon nitride, boron nitride, silicon carbide, and boron carbide. The alkali-resistant ceramics preferably contains at least one selected from the group consisting of tantalum oxide, aluminum oxide, tantalum nitride, aluminum nitride, silicon nitride, boron nitride, silicon carbide, and boron carbide. The preparation of a coating film of the alkali-resistant ceramics on a conductive substrate is possible with, but not limited to, a combination of sintering and vapor phase plating or of vapor phase plating and anodic oxidation. In addition, the conductive substrate can be subjected to suitable pretreatment such as etching for the purpose of obtaining adhesion by the anchor effect. In this case, the arithmetic average roughness (Ra) of the surface is preferably 3 to 4 μm , for example. Note that the top of the coating film of the alkali-resistant ceramics may be coated with an ion exchange resin or the like.

[0016] The film thickness of the coating film of the alkali-resistant ceramics is preferably approximately 0.1 to 50 μm and particularly preferably 0.5 to 1 μm . The conductivity decreases when the film thickness is too thick, and the decomposition suppression effect decreases when the film thickness is too thin. The above preparation method may be carried out more than once to set the total film thickness of the coating film of the alkali-resistant ceramics in the above ranges. The pore diameter in the coating film of the alkali-resistant ceramics is preferably approximately 0.1 to 5 μm and further preferably 0.1 to 1 μm . The decomposition suppression effect decreases when the pore diameter exceeds 5 μm . Here, the conductive state means a state where ions and the like can transfer through the above-described pores, cracks, and the like.

[0017] The conductive substrate is preferably one coated with iron, nickel, stainless steel, carbon, titanium, zirconium, niobium, tantalum, platinum, platinum-plated titanium, palladium-tin alloy, or these, but is not limited to the above as long as the conductive substrate is conductive. The conductive substrate is more preferably contains at least one of nickel and iron.

[0018] The anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics is preferably an anode composed of a conductive substrate and an alkali-resistant ceramics coating.

[0019] The alkaline zinc electroplating bath used in the present invention is an alkaline zinc plating bath containing an organic compound additive. The alkaline zinc electroplating bath preferably contains one or more organic compound additives selected from the group consisting of brightening agents, auxiliary additives such as leveling agents, and defoamers. The alkaline zinc electroplating bath is preferably one containing a brightening agent.

[0020] The alkaline zinc alloy electroplating bath used in the present invention is an alkaline zinc alloy electroplating bath containing an amine chelating agent and an organic compound additive. The alkaline zinc alloy electroplating bath preferably contains an amine chelating agent and one or more organic compound additives selected from the group consisting of brightening agents, auxiliary additives such as leveling agents, and defoamers. The alkaline zinc alloy electroplating bath preferably contains a brightening agent.

[0021] No particular limitation is imposed on the brightening agent as long as it is a brightening agent known in zinc plating baths, and examples thereof include (1) nonionic surfactants such as polyoxyethylene polyoxypropylene block polymers and acetylene glycol EO adducts and anionic surfactants such as polyoxyethylene lauryl ether sulfate and alkyl diphenyl ether disulfonate (2) polyamine compounds such as; polyallylamines such as copolymers of diallyldimethylammonium chloride and sulfur dioxide; polyepoxy polyamines such as condensation polymers of ethylene diamine and epichlorohydrin, condensation polymers of dimethylaminopropylamine and epichlorohydrin, condensation polymers of imidazole and epichlorohydrin, condensation polymers of epichlorohydrin and imidazole derivatives such as 1-methylimidazole and 2-methylimidazole, and condensation polymers of epichlorohydrin and heterocyclic amines containing triazine derivatives such as acetoguanamine and benzoguanamine polyamide polyamines including polyamine polyurea resins such as condensation polymers of 3-dimethylaminopropyl urea and epichlorohydrin and condensation polymers of bis(N,N-dimethylaminopropyl)urea and epichlorohydrin and water-soluble nylon resins such as condensation polymers of N,N-dimethylaminopropylamine, alkylene dicarboxylic acids, and epichlorohydrin polyalkylene polyamines such as condensation polymers of 2,2'-dichlorodiethyl ether with diethylenetriamine, dimethylaminopropylamine, and the like, condensation polymers of dimethylaminopropylamine and 1,3-dichloropropane, condensation polymers of N,N,N',N'-tetramethyl-1,3-diaminopropane and 1,4-dichlorobutane, and condensation polymers of N,N,N',N'-tetramethyl-1,3-diaminopropane and 1,3-dichloropropan-2-ol (3) condensation polymers of dichloroethyl ether with dimethylamine and

the like (4) aromatic aldehydes such as veratraldehyde, vanillin, and anisaldehyde and benzoic acids or salts thereof and (5) quaternary ammonium salts such as cetyltrimethylammonium chloride, 3-carbamoylbenzyl chloride, and pyridinium. Among these, quaternary ammonium salts and aromatic aldehydes are preferable. These brightening agents may be used alone or in combination of two or more. The concentration of the brightening agent in the alkaline zinc or zinc alloy electroplating bath is preferably 1 to 500 mg/L and further preferably 5 to 100 mg/L in the case of aromatic aldehydes and benzoic acids or salts thereof, and is preferably 0.01 to 10 g/L and further preferably 0.02 to 5 g/L in other cases.

[0022] In addition, the brightening agent may be a nitrogen-containing heterocyclic quaternary ammonium salt. The nitrogen-containing heterocyclic quaternary ammonium salt brightening agent is more preferably a carboxy group- and/or hydroxy group-substituted nitrogen-containing heterocyclic quaternary ammonium salt. Examples of the nitrogen-containing heterocyclic quaternary ammonium salt include pyridine rings, piperidine rings, imidazole rings, imidazoline rings, pyrrolidine rings, pyrazole rings, quinoline rings, and morpholine rings, and the nitrogen-containing heterocyclic quaternary ammonium salt is preferably a pyridine ring and particularly preferably a quaternary ammonium salt of nicotinic acid or a derivative thereof. In the quaternary ammonium salt compound, the carboxy group and/or hydroxy group may be a substituent in a nitrogen-containing heterocyclic quaternary ammonium salt as in the case of a carboxymethyl group. In addition, the nitrogen-containing heterocyclic quaternary ammonium salt may have a substituent such as an alkyl group other than the carboxy group and/or hydroxy group. In addition, the N-substituent forming the heterocyclic quaternary ammonium cation is not particularly limited as long as the brightening agent-containing effect is not inhibited, and examples thereof include substituted or non-substituted alkyl groups, aryl groups, and alkoxy groups. In addition, examples of counter anions which form salts include compounds containing halogen anions, oxy anions, borate anions, sulfonate anions, phosphate anions, and imido anions, and halogen anions are preferable. Such quaternary ammonium salts are preferable because they both contain quaternary ammonium cations and oxyanions in the molecule and thus exhibit behavior as negative ions. Specific examples of nitrogen-containing heterocyclic quaternary ammonium salt compounds include N-benzyl-3-carboxypyridinium chloride, N-phenethyl-4-carboxypyridinium chloride, N-butyl-3-carboxypyridinium bromide, N-chloromethyl-3-carboxypyridinium bromide, N-hexyl-6-hydroxy-3-carboxypyridinium chloride, N-hexyl-6-3-hydroxypropyl-3-carboxypyridinium chloride, N-2-hydroxyethyl-6-methoxy-3-carboxypyridinium chloride, N-methoxy-6-methyl-3-carboxypyridinium chloride, N-propyl-2-methyl-6-phenyl-3-carboxypyridinium chloride, N-propyl-2-methyl-6-phenyl-3-carboxypyridinium chloride, N-benzyl-3-carboxymethyl pyridinium chloride, 1-butyl-3-methyl-4-carboxy imidazolium bromide, 1-butyl-3-methyl-4-carboxymethyl imidazolium bromide, 1-butyl-2-hydroxymethyl-3-methylimidazolium chloride, 1-butyl-1-methyl-3-methylcarboxypyrrolidinium chloride, and 1-butyl-1-methyl-4-methylcarboxypiperidinium chloride. These nitrogen-containing heterocyclic quaternary ammonium salts may be used alone or in combination of two or more. The concentration of the nitrogen-containing heterocyclic quaternary ammonium salt in the alkaline zinc or zinc alloy electroplating bath is preferably 0.01 to 10 g/L and further preferably 0.02 to 5 g/L.

[0023] Examples of auxiliary additives include organic acids, silicates, and mercapto compounds. These auxiliary additives may be used alone or in combination of two or more. The concentration of the auxiliary additive in the alkaline zinc or zinc alloy electroplating bath is preferably 0.01 to 50 g/L.

[0024] Examples of defoamers include surfactants. These defoamers may be used alone or in combination of two or more. The concentration of the defoamer in the alkaline zinc or zinc alloy electroplating bath is preferably 0.01 to 5 g/L.

[0025] Examples of amine chelating agents include alkylene amine compounds such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and pentaethylenhexamine; alkylene oxide adducts such as ethylene oxide adducts and propylene oxide adducts of the above alkylene amines; aminoalcohols such as ethanolamine, diethanolamine, triethanolamine, diisopropanolamine, triisopropanolamine, ethylenediamine tetra-2-propanol, N-(2-aminoethyl)ethanolamine, and 2-hydroxyethylaminopropylamine; alkanolamine compounds such as N-(2-hydroxyethyl)-N,N',N'-triethylethylenediamine, N,N'-di(2-hydroxyethyl)-N,N'-diethylethylenediamine, N,N,N',N'-tetrakis(2-hydroxyethyl)propylenediamine, and N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine; poly(alkylene imine) obtained from ethylene imine, 1,2-propylene imine, and the like; and poly(alkylene amine) obtained from ethylene diamine, triethylene tetramine, and the like. The amine chelating agent preferably contains one or more selected from the group consisting of alkylene amine compounds, alkylene oxide adducts thereof, and alkanolamine compound. These amine chelating agents may be used alone or in combination of two or more. The concentration of the amine chelating agent in the alkaline zinc or zinc alloy electroplating bath is preferably 5 to 200 g/L and more preferably 30 to 100 g/L.

[0026] The alkaline zinc or zinc alloy electroplating bath used in the present invention contains zinc ions. The concentration of the zinc ions in the alkaline zinc or zinc alloy electroplating bath is preferably 2 to 20 g/L or more preferably 4 to 12 g/L. Examples of zinc ion sources include $\text{Na}_2[\text{Zn}(\text{OH})_4]$, $\text{K}_2[\text{Zn}(\text{OH})_4]$, and ZnO. These zinc ion sources may be used alone or in combination of two or more.

[0027] The alkaline zinc or zinc alloy electroplating bath used in the present invention preferably contains caustic alkali. Examples of caustic alkalis include sodium hydroxide and potassium hydroxide, and sodium hydroxide is preferable. The concentration of the caustic alkali in the alkaline zinc or zinc alloy electroplating bath is preferably 60 to 200 g/L and more preferably 100 to 160 g/L.

[0028] The alkaline zinc alloy electroplating bath used in the present invention contains ions of metal other than zinc. As the above metal ions, the alkaline zinc alloy electroplating bath preferably contains one or more kind of metal ions selected from the group consisting of nickel ions, iron ions, cobalt ions, tin ions, and manganese ions. The total concentration of the metal ions in the alkaline zinc alloy electroplating bath is preferably 0.4 to 4 g/L and more preferably 1 to 3 g/L. Examples of metal ion sources include nickel sulfate, ferrous sulfate, cobalt sulfate, stannous sulfate, and manganese sulfate. These metal ion sources may be used alone or in combination of two or more. The alkaline zinc alloy electroplating bath used in the present invention is preferably an alkaline zinc nickel alloy electroplating bath containing nickel ions as the above metal ions.

[0029] The alkaline zinc electroplating bath is preferably an alkaline zinc electroplating bath at least containing zinc ions, caustic alkali, and an organic compound additive.

[0030] The alkaline zinc alloy electroplating bath is preferably an alkaline zinc alloy electroplating bath at least containing zinc ions, metal ions, caustic alkali, an amine chelating agent, and an organic compound additive, and the metal ions include at least one kind selected from the group consisting of nickel ions, iron ions, cobalt ions, tin ions, and manganese ions.

[0031] The temperature during the zinc or zinc alloy plating is preferably 15°C to 40°C and further preferably 25 to 35°C. The cathode current density during the zinc or zinc alloy plating is preferably 0.1 to 20 A/dm² and further preferably 0.2 to 10 A/dm².

[0032] Next, the present invention is described with reference to Examples and Comparative Examples, but the invention is not limited to these.

[Examples]

(Example 1)

[0033] An anode plate (surface roughness Ra: 4 μm, 64 × 64 × 2 mm) coated with tantalum oxide in a thickness of 0.5 to 0.8 μm on Ni was used and an alkaline zinc nickel alloy plating bath shown below was used (500 mL) to carry out zinc nickel alloy plating with energizing of 500 Ah/L. The pore diameter in the coating film was 0.1 to 1 μm, and the drag-out of the plating bath was set to 2 mL/Ah. The cathode current density was 4 A/dm², the anode current density was 9.8 A/dm², and the plating bath temperature was 25°C. The plating bath was cooled to maintain 25°C. An iron plate was used as the cathode. Note that the iron plate of the cathode was replaced for each 16 Ah/L during the energizing. The zinc ion concentration of the plating bath was kept constant by immersion and dissolution of the metal zinc. The nickel ion concentration of the plating bath was kept constant by replenishing a nickel replenishment agent IZ-250YNi (manufactured by Dipsol). The caustic soda concentration of the plating bath was periodically analyzed and replenished to a constant concentration. The brightening agents replenished were polyamine IZ-250YR1 (manufactured by Dipsol) and nitrogen-containing heterocyclic quaternary ammonium salt IZ-250YR2 (manufactured by Dipsol) at replenishing rates of 15 mL/kAh and 15 mL/kAh, respectively. The amine chelating agent IZ-250YB was replenished at an IZ-250YB replenishing rate of 80 mL/kAh. The concentration of the amine chelating agent, the oxalic acid concentration, and the cyan concentration in the catholyte were analyzed for each energizing of 250 Ah/L. In addition, the presence or absence of precipitate was visually observed. Table 1 shows the results. Moreover, the chelating agent concentration was set to the initial concentration during the energizing of 500 Ah/L and a long cell having a 20 cm iron plate as the cathode was used for a plating test in accordance with the hull cell test to measure the plating appearance, the film thickness distribution, and the Ni co-deposition ratio distribution. Fig. 1, Fig. 6, and Fig. 7 show the respective results. Note that the conditions for the plating test in accordance with the hull cell test were 4A-20 minutes and 25°C. In addition, the surface of the anode was observed to check the presence or absence of film peeling. Table 1 shows the results.

Composition of Plating Solution:

Zn ion concentration 8 g/L (Zn ion source is Na₂[Zn(OH)₄])

Ni ion concentration 1.6 g/L (Ni ion source is NiSO₄·6H₂O)

caustic soda concentration 130 g/L

amine chelating agent (ethylene oxide adduct of an alkylene amine) IZ-250YB (manufactured by Dipsol) 60 g/L

brightening agent IZ-250YR1 (manufactured by Dipsol) 0.6 mL/L (polyamine 0.1 g/L)

brightening agent IZ-250YR2 (manufactured by Dipsol) 0.5 mL/L (0.2 g/L of quaternary ammonium salt of nicotinic acid)

(Example 2)

[0034] An anode plate (surface roughness Ra: 4 μm, 64 × 64 × 2 mm) coated with tantalum oxide in a thickness of 0.5 to 0.8 μm on Fe was used and an alkaline zinc nickel alloy plating bath shown below was used (500 mL) to carry

out zinc nickel alloy plating with energizing of 500 Ah/L. The pore diameter in the coating film was 0.1 to 1 μm , and the drag-out of the plating bath was set to 2 mL/Ah. The cathode current density was 4 A/dm², the anode current density was 9.8 A/dm², and the plating bath temperature was 25°C. The plating bath was cooled to maintain 25°C. An iron plate was used as the cathode. Note that the iron plate of the cathode was replaced for each 16 Ah/L during the energizing.

The zinc ion concentration of the plating bath was kept constant by immersion and dissolution of the metal zinc. The nickel ion concentration of the plating bath was kept constant by replenishing a nickel replenishment agent IZ-250YNi (manufactured by Dipsol). The caustic soda concentration of the plating bath was periodically analyzed and replenished to a constant concentration. The brightening agents replenished were polyamine IZ-250YR1 (manufactured by Dipsol) and nitrogen-containing heterocyclic quaternary ammonium salt IZ-250YR2 (manufactured by Dipsol) at replenishing rates of 15 mL/kAh and 15 mL/kAh, respectively. The amine chelating agent IZ-250YB was replenished at an IZ-250YB replenishing rate of 80 mL/kAh. The concentration of the amine chelating agent, the oxalic acid concentration, and the cyan concentration in the catholyte were analyzed for each energizing of 250 Ah/L. In addition, the presence or absence of precipitate was visually observed. Table 1 shows the results. Moreover, the chelating agent concentration was set to the initial concentration during the energizing of 500 Ah/L and a long cell having a 20 cm iron plate as the cathode was used for a plating test in accordance with the hull cell test to measure the plating appearance, the film thickness distribution, and the Ni co-deposition ratio distribution. Fig. 2, Fig. 8, and Fig. 9 show the respective results. Note that the conditions for the plating test in accordance with the hull cell test were 4A-20 minutes and 25°C. In addition, the surface of the anode was observed to check the presence or absence of film peeling. Table 1 shows the results.

Composition of Plating Solution:

[0035]

Zn ion concentration 8 g/L (Zn ion source is $\text{Na}_2[\text{Zn}(\text{OH})_4]$)
 Ni ion concentration 1.6 g/L (Ni ion source is $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)
 caustic soda concentration 130 g/L
 amine chelating agent (ethylene oxide adduct of an alkylene amine) IZ-250YB (manufactured by Dipsol) 60 g/L
 brightening agent IZ-250YR1 (manufactured by Dipsol) 0.6 mL/L (polyamine 0.1 g/L)
 brightening agent IZ-250YR2 (manufactured by Dipsol) 0.5 mL/L (0.2 g/L of quaternary ammonium salt of nicotinic acid)

(Example 3)

[0036] An anode plate (surface roughness Ra: 4 μm , 64 × 64 × 2 mm) coated with tantalum oxide in a thickness of 0.5 to 0.8 μm on Ni was used and an alkaline zinc nickel alloy plating bath shown below was used (500 mL) to carry out zinc nickel alloy plating with energizing of 500 Ah/L. The pore diameter in the coating film was 0.1 to 1 μm , and the drag-out of the plating bath was set to 2 mL/Ah. The cathode current density was 2 A/dm², the anode current density was 4.9 A/dm², and the plating bath temperature was 25°C. The plating bath was cooled to maintain 25°C. An iron plate was used as the cathode. Note that the iron plate of the cathode was replaced for each 16 Ah/L during the energizing. The zinc ion concentration of the plating bath was kept constant by immersion and dissolution of the metal zinc. The nickel ion concentration of the plating bath was kept constant by replenishing a nickel replenishment agent IZ-250YNi (manufactured by Dipsol). The caustic soda concentration of the plating bath was periodically analyzed and replenished to a constant concentration. The brightening agents replenished were polyamine IZ-250YR1 (manufactured by Dipsol) and nitrogen-containing heterocyclic quaternary ammonium salt IZ-250YR2 (manufactured by Dipsol) at replenishing rates of 15 mL/kAh and 15 mL/kAh, respectively. The amine chelating agent tetraethylenepentamine was replenished at a replenishing rate of 40 mL/kAh. The concentration of the amine chelating agent and the cyan concentration in the catholyte were analyzed for each energizing of 250 Ah/L. In addition, the presence or absence of precipitate was visually observed. Table 2 shows the results. Moreover, the chelating agent concentration was set to the initial concentration during the energizing of 500 Ah/L and a long cell having a 20 cm iron plate as the cathode was used for a plating test in accordance with the hull cell test to measure the plating appearance, the film thickness distribution, and the Ni co-deposition ratio distribution. Fig. 3, Fig. 10, and Fig. 11 show the respective results. Note that the conditions for the plating test in accordance with the hull cell test were 2A-20 minutes and 25°C.

Composition of Plating Solution:

[0037]

Zn ion concentration 8 g/L (Zn ion source is $\text{Na}_2[\text{Zn}(\text{OH})_4]$)

Ni ion concentration 1.2 g/L (Ni ion source is $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)

caustic soda concentration 130 g/L

amine chelating agent (tetraethylenepentamine) 30 g/L

brightening agent IZ-250YR1 (manufactured by Dipsol) 0.6 mL/L (polyamine 0.1 g/L)

brightening agent IZ-250YR2 (manufactured by Dipsol) 0.5 mL/L (0.2 g/L of quaternary ammonium salt of nicotinic acid)

(Comparative Example 1)

[0038] An alkaline zinc nickel alloy plating bath shown below was used (500 mL) to carry out zinc nickel alloy plating with energizing of 500 Ah/L. The drag-out of the plating bath was set to 2 mL/Ah. The cathode current density was 4 A/dm², the anode current density was 9.8 A/dm², and the plating bath temperature was 25°C. The plating solution was cooled to maintain 25°C. An iron plate was used as the cathode, and a nickel plate was used as the anode. Note that the iron plate of the cathode was replaced for each 16 Ah/L during the energizing. The zinc ion concentration of the plating bath was kept constant by immersion and dissolution of the metal zinc. The nickel ion concentration of the plating bath was kept constant by replenishing a nickel replenishment agent IZ-250YNi (manufactured by Dipsol). The caustic soda concentration of the plating bath was periodically analyzed and replenished to a constant concentration. The brightening agents replenished were polyamine IZ-250YR1 (manufactured by Dipsol) and nitrogen-containing heterocyclic quaternary ammonium salt IZ-250YR2 (manufactured by Dipsol) at replenishing rates of 15 mL/kAh and 15 mL/kAh, respectively. The amine chelating agent IZ-250YB was replenished at an IZ-250YB replenishing rate of 80 mL/kAh. The concentration of the amine chelating agent, the oxalic acid concentration, and the cyan concentration were analyzed for each energizing of 250 Ah/L. In addition, the presence or absence of precipitate was visually observed. Table 1 shows the results. Moreover, the chelating agent concentration was set to the initial concentration during the energizing of 500 Ah/L and a long cell having a 20 cm iron plate as the cathode was used for a plating test in accordance with the hull cell test to measure the plating appearance, the film thickness distribution, and the Ni co-deposition ratio distribution. Fig. 4, Fig. 12, and Fig. 13 show the respective results. Note that the conditions for the plating test in accordance with the hull cell test were 4A-20 minutes and 25°C.

Composition of Plating Solution:

[0039]

Zn ion concentration 8 g/L (Zn ion source is $\text{Na}_2[\text{Zn}(\text{OH})_4]$)

Ni ion concentration 1.6 g/L (Ni ion source is $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)

caustic soda concentration 130 g/L

amine chelating agent (ethylene oxide adduct of an alkylene amine) IZ-250YB (manufactured by Dipsol) 60 g/L

brightening agent IZ-250YR1 (manufactured by Dipsol) 0.6 mL/L (polyamine 0.1 g/L)

brightening agent IZ-250YR2 (manufactured by Dipsol) 0.5 mL/L (0.2 g/L of quaternary ammonium salt of nicotinic acid)

(Comparative Example 2)

[0040] An anode plate (surface roughness Ra: 4 μm , 64 × 64 × 2 mm) coated with iridium oxide in a thickness of 0.5 to 0.8 μm on Pt/Ti was used and an alkaline zinc nickel alloy plating bath shown below was used (500 mL) to carry out zinc nickel alloy plating with a energizing of 500 Ah/L. The pore diameter in the coating film was 0.1 to 1 μm , and the drag-out of the plating bath was set to 2 mL/Ah. The cathode current density was 4 A/dm², the anode current density was 9.8 A/dm², and the plating bath temperature was 25°C. The plating bath was cooled to maintain 25°C. An iron plate was used as the cathode. Note that the iron plate of the cathode was replaced for each 16 Ah/L during the energizing. The zinc ion concentration of the plating bath was kept constant by immersion and dissolution of the metal zinc. The nickel ion concentration of the plating bath was kept constant by replenishing a nickel replenishment agent IZ-250YNi (manufactured by Dipsol). The caustic soda concentration of the plating bath was periodically analyzed and replenished to a constant concentration. The brightening agents replenished were polyamine IZ-250YR1 (manufactured by Dipsol) and nitrogen-containing heterocyclic quaternary ammonium salt IZ-250YR2 (manufactured by Dipsol) at replenishing rates of 15 mL/kAh and 15 mL/kAh, respectively. The amine chelating agent IZ-250YB was replenished at an IZ-250YB replenishing rate of 80 mL/kAh. The concentration of the amine chelating agent, the oxalic acid concentration, and the cyan concentration in the catholyte were analyzed for each energizing of 250 Ah/L. In addition, the presence or absence of precipitate was visually observed. Table 1 shows the results. Moreover, the chelating agent concentration was set to the initial concentration during the energizing of 500 Ah/L and a long cell having a 20 cm iron plate as the cathode was

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used for a plating test in accordance with the hull cell test to measure the plating appearance, the film thickness distribution, and the Ni co-deposition ratio distribution. Fig. 5, Fig. 14, and Fig. 15 show the respective results. Note that the conditions for the plating test in accordance with the hull cell test were 4A-20 minutes and 25°C. In addition, the surface of the anode was observed to check the presence or absence of film peeling. Table 1 shows the results.

Composition of Plating Solution:

[0041]

Zn ion concentration 8 g/L (Zn ion source is $\text{Na}_2[\text{Zn}(\text{OH})_4]$)
 Ni ion concentration 1.6 g/L (Ni ion source is $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)
 caustic soda concentration 130 g/L
 amine chelating agent (ethylene oxide adduct of an alkylene amine) IZ-250YB (manufactured by Dipsol) 60 g/L
 brightening agent IZ-250YR1 (manufactured by Dipsol) 0.6 mL/L (polyamine 0.1 g/L)
 brightening agent IZ-250YR2 (manufactured by Dipsol) 0.5 mL/L (0.2 g/L of quaternary ammonium salt of nicotinic acid)

[0042] Table 1 Transition of Concentration of Amine Chelating Agent, Oxalic Acid Concentration, and Cyan Concentration as Well as Presence or Absence of Deposits and Film Peeling

[Table 1]

	Energizing Quantity (Ah/L)	Amine Chelating Agent (g/L)	Oxalic Acid (g/L)	Cyan (mg/L)	Deposit	Film Peeling
Initially	0	60	0	< 2	None	-
Example 1	250	59	0.2	< 2	None	None
	500	57	0.5	< 2	None	None
Example 2	250	58	0.3	< 2	None	None
	500	55	0.8	< 2	None	None
Comparative Example 1	250	40	1.7	15	Yes	-
	500	35	2.0	30	Yes	-
Comparative Example 2	250	38	2.0	25	Yes	Yes
	500	30	2.4	40	Yes	Yes

[0043] Table 2 Transition of Concentration of Amine Chelating Agent and Cyan Concentration as Well as Presence or Absence of Deposits

[Table 2]

	Energizing Quantity (Ah/L)	Amine Chelating Agent (g/L)	Cyan (mg/L)	Deposit
Initially	0	30	< 2	None
Example 3	250	28	< 2	None
	500	27	< 2	None

[0044] Example 1 to 3 showed the following effects as compared with Comparative Examples 1 and 2.

- (1) The decomposition of the amine chelating agent was suppressed.
- (2) The lowering of the plating appearance was suppressed.
- (3) The decrease in plating rate was suppressed.
- (4) The decrease in Ni co-deposition ratio was suppressed.

[0045] The present invention made it possible to achieve lifetime extension of an alkaline zinc or zinc alloy plating

bath, particularly an alkaline zinc nickel alloy plating bath. In addition, the lifetime extension of an alkaline zinc or zinc alloy plating bath, particularly an alkaline zinc nickel alloy plating bath made it possible to stabilize the plating quality, shorten the plating time, and reduce the burden of wastewater treatment.

5

Claims

1. A zinc or zinc alloy electroplating method comprising:

10 performing energizing in an alkaline zinc or zinc alloy electroplating bath provided with a cathode and an anode, wherein the anode is an anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics, the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc plating bath containing an organic compound additive or an alkaline zinc alloy electroplating bath containing an amine chelating agent or an organic compound additive, 15 oxidation decomposition, on a surface of the anode caused by the energizing, of the organic compound additive in the alkaline zinc plating bath or the amine chelating agent and the organic compound additive in the alkaline zinc alloy electroplating bath is suppressed as compared with a case of using as an anode of the same conductive substrate uncoated with the alkali-resistant ceramics. 20

2. The zinc or zinc alloy electroplating method according to claim 1, wherein the anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics consists of a conductive substrate and an alkali-resistant ceramics coating. 25

3. The zinc or zinc alloy electroplating method according to claim 1 or 2, wherein the conductive substrate contains at least one of nickel and iron.

4. The zinc or zinc alloy electroplating method according to any one of claims 1 to 3, wherein the alkali-resistant ceramics contain at least one selected from the group consisting of tantalum oxide, aluminum oxide, tantalum nitride, aluminum nitride, silicon nitride, boron nitride, silicon carbide, and boron carbide. 30

5. The zinc or zinc alloy electroplating method according to any one of claims 1 to 4, wherein the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc electroplating bath at least containing zinc ions, caustic alkali, and an organic compound additive. 35

6. The zinc or zinc alloy electroplating method according to any one of claims 1 to 4, wherein

the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc alloy electroplating bath at least containing zinc ions, metal ions, caustic alkali, an amine chelating agent, and an organic compound additive, and the metal ions include at least one selected from the group consisting of nickel ions, iron ions, cobalt ions, tin ions, and manganese ions. 40

7. The zinc or zinc alloy electroplating method according to claim 6, wherein the amine chelating agent contains at least one selected from the group consisting of alkylene amine compounds, alkylene oxide adducts thereof, and alkanolamine compounds. 45

8. A zinc or zinc alloy electroplating system comprising:

50 an alkaline zinc or zinc alloy electroplating bath provided with a cathode and an anode, wherein the anode is an anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics, the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc plating bath containing an organic compound additive or an alkaline zinc alloy electroplating bath containing an amine chelating agent or an organic compound additive, 55 oxidation decomposition, on a surface of the anode caused by the energizing, of the organic compound additive in the alkaline zinc plating bath or the amine chelating agent and the organic compound additive in the alkaline zinc alloy electroplating bath is suppressed as compared with a case of using as an anode of the same conductive

substrate uncoated with the alkali-resistant ceramics.

9. The zinc or zinc alloy electroplating system according to claim 8, wherein
the anode in which a conductive substrate is coated in a conductive state with alkali-resistant ceramics consists of
a conductive substrate and an alkali-resistant ceramics coating.
10. The zinc or zinc alloy electroplating system according to claim 8 or 9, wherein
the conductive substrate contains at least one of nickel and iron.
11. The zinc or zinc alloy electroplating method according to any one of claims 8 to 10, wherein
the alkali-resistant ceramics contain at least one selected from the group consisting of tantalum oxide, aluminum
oxide, tantalum nitride, aluminum nitride, silicon nitride, boron nitride, silicon carbide, and boron carbide.
12. The zinc or zinc alloy electroplating method according to any one of claims 8 to 11, wherein
the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc electroplating bath at least containing zinc ions,
caustic alkali, and an organic compound additive.
13. The zinc or zinc alloy electroplating method according to any one of claims 8 to 11, wherein
the alkaline zinc or zinc alloy electroplating bath is an alkaline zinc alloy electroplating bath at least containing
zinc ions, metal ions, caustic alkali, an amine chelating agent, and an organic compound additive, and
the metal ions include at least one selected from the group consisting of nickel ions, iron ions, cobalt ions, tin
ions, and manganese ions.
14. The zinc or zinc alloy electroplating method according to claim 13, wherein
the amine chelating agent contains at least one selected from the group consisting of alkylene amine compounds,
alkylene oxide adducts thereof, and alkanolamine compounds.

FIG.1

EXAMPLE 1

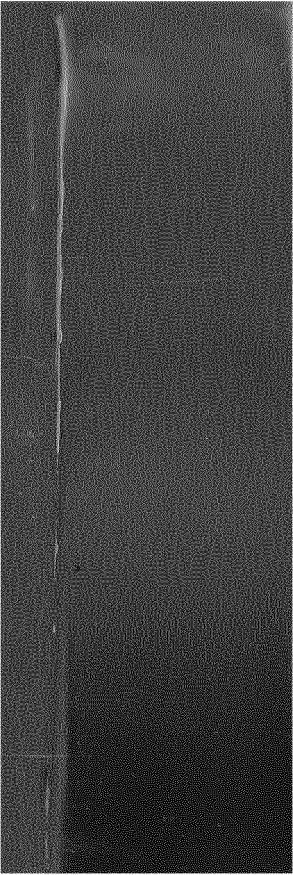
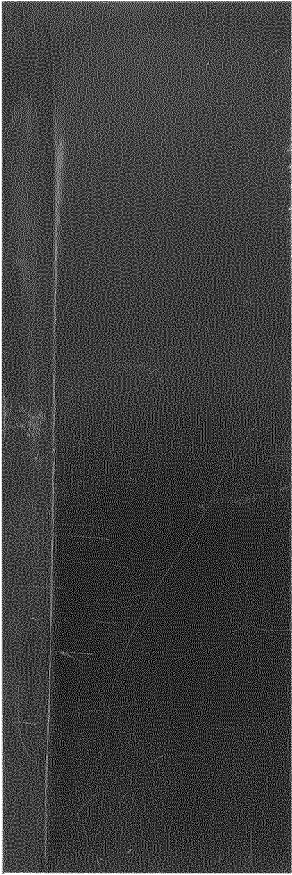
ENERGIZING QUANTITY	DISTANCE FROM LEFT END OF HULL CELL (cm)	1	2	3	5	7	9	11	13	15	17	19
0 Ah/L	FILM THICKNESS(μm)	17.1	13.1	10.7	7.4	5.3	3.1	1.9	1.1	0.7	0.4	0.2
	Ni(%)	15.7	15.6	15.6	15.6	15.4	15.5	15.5	15.6	14.9	14.5	15.2
	HULL CELL APPEARANCE											
500 Ah/L	FILM THICKNESS(μm)	17.3	13.0	10.4	7.3	5.6	3.5	2.1	1.1	0.7	0.5	0.2
	Ni(%)	15.4	15.4	15.5	15.7	15.6	15.8	15.7	15.5	14.8	14.5	14.7
	HULL CELL APPEARANCE											

FIG.2
EXAMPLE 2

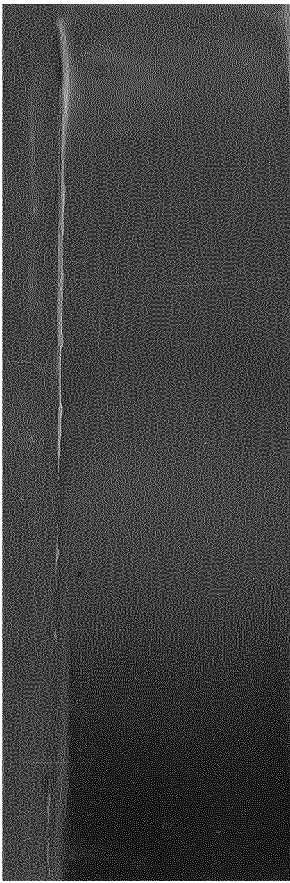
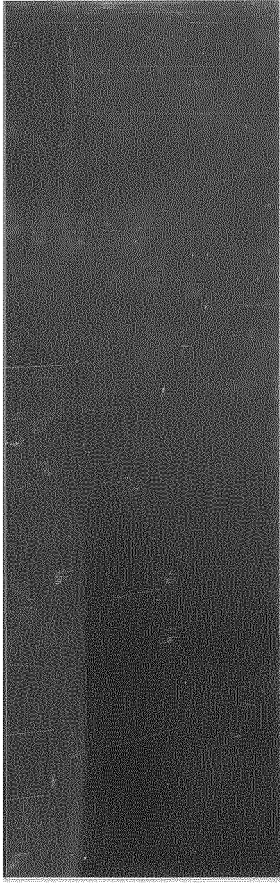
ENERGIZING QUANTITY	DISTANCE FROM LEFT END OF HULL CELL (cm)	1	2	3	5	7	9	11	13	15	17	19
0 Ah/L	FILM THICKNESS(μm)	17.1	13.1	10.7	7.4	5.3	3.1	1.9	1.1	0.7	0.4	0.2
	Ni(%)	15.7	15.6	15.6	15.6	15.4	15.5	15.5	15.6	14.9	14.5	15.2
	HULL CELL APPEARANCE											
500 Ah/L	FILM THICKNESS(μm)	16.8	12.8	10.3	7.0	5.6	3.0	2.0	1.2	0.8	0.5	0.4
	Ni(%)	15.2	15.3	15.2	15.2	15.3	15.2	15.5	15.3	14.9	14.7	14.1
	HULL CELL APPEARANCE											

FIG.3

EXAMPLE 3


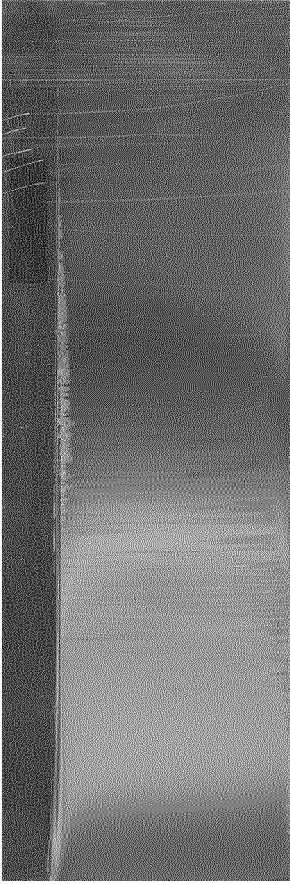
ENERGIZING QUANTITY	DISTANCE FROM LEFT END OF HULL CELL (cm)	1	2	3	5	7	9	11	13	15	17	19
0 Ah/L	FILM THICKNESS(μm)	19.1	15.2	12.6	7.3	4.6	2.7	1.7	1.1	0.8	0.6	0.5
	Ni(%)	15.0	14.6	14.2	13.7	14.3	14.7	15.4	15.9	15.8	14.8	14.8
	HULL CELL APPEARANCE											
500 Ah/L	FILM THICKNESS(μm)	18.8	15.0	12.3	7.5	4.3	2.6	1.8	1.1	0.9	0.5	0.4
	Ni(%)	14.9	14.4	14.0	13.5	14.0	14.5	14.9	15.5	15.5	14.5	14.6
	HULL CELL APPEARANCE											

FIG.4

COMPARATIVE EXAMPLE 1

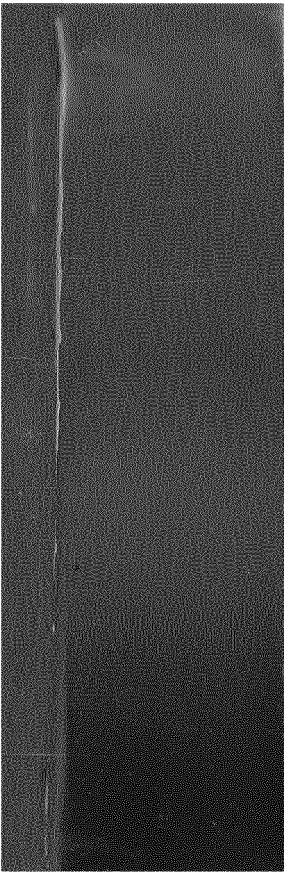
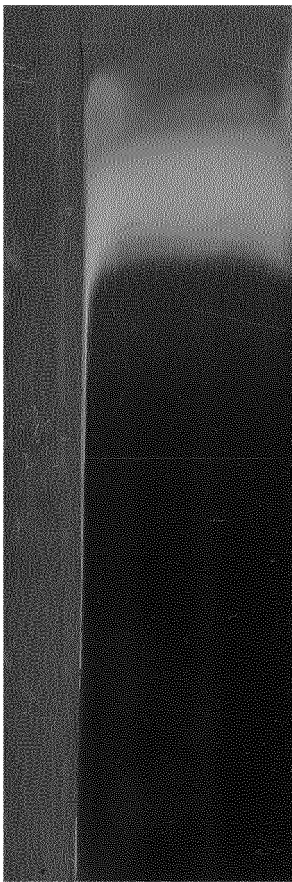
ENERGIZING QUANTITY	DISTANCE FROM LEFT END OF HULL CELL (cm)	1	2	3	5	7	9	11	13	15	17	19
0 Ah/L	FILM THICKNESS(μm)	17.1	13.1	10.2	7.4	5.3	3.1	1.9	1.1	0.7	0.4	0.2
	Ni(%)	15.7	15.6	15.6	15.6	15.4	15.5	15.5	15.6	14.9	14.5	15.2
	HULL CELL APPEARANCE											
500 Ah/L	FILM THICKNESS(μm)	13.9	11.0	8.8	6.5	4.8	3.0	1.7	1.0	0.6	0.5	0.3
	Ni(%)	14.4	14.3	14.2	14.5	14.8	14.8	14.6	14.6	14.2	14.0	12.7
	HULL CELL APPEARANCE											

FIG.5
COMPARATIVE EXAMPLE 2

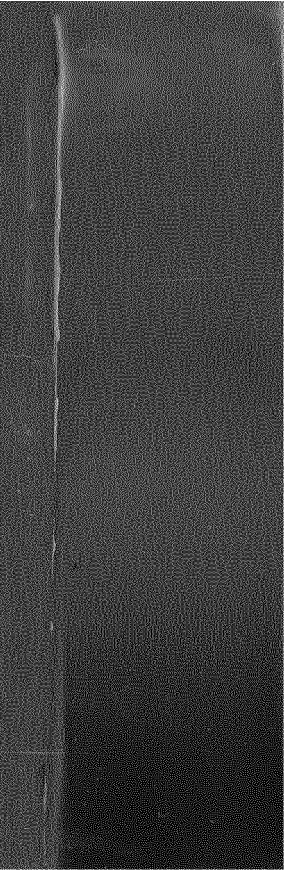
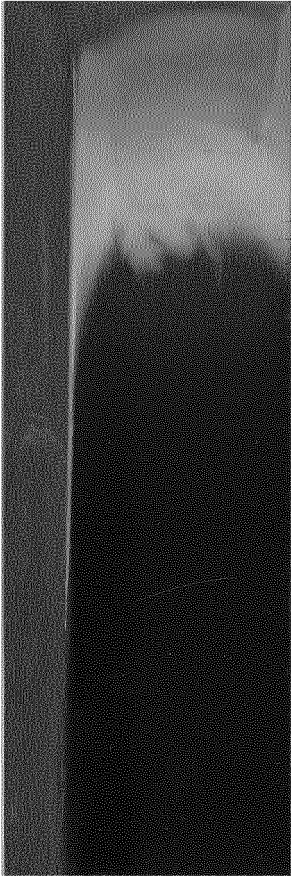
ENERGIZING QUANTITY	DISTANCE FROM LEFT END OF HULL CELL (cm)	1	2	3	5	7	9	11	13	15	17	19
	FILM THICKNESS(μm)	17.1	13.1	10.2	7.4	5.3	3.1	1.9	1.1	0.7	0.4	0.2
	Ni(%)	15.7	15.6	15.6	15.6	15.4	15.5	15.5	15.6	14.9	14.5	15.2
	HULL CELL APPEARANCE											
500 Ah/L	FILM THICKNESS(μm)	13.5	10.7	8.5	6.3	4.6	2.8	1.6	1.0	0.7	0.5	0.3
	Ni(%)	14.5	14.7	14.8	15.1	15.0	14.9	14.4	14.2	14.1	14.1	14.5
	HULL CELL APPEARANCE											

FIG.6

EXAMPLE 1 FILM THICKNESS DISTRIBUTION

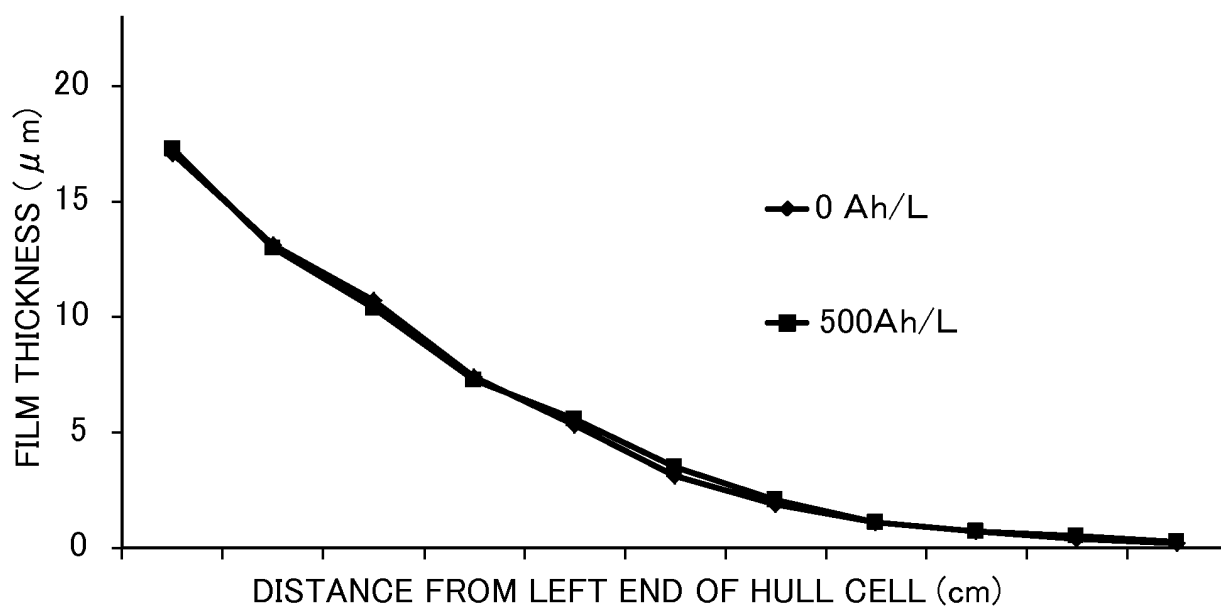


FIG.7

EXAMPLE 1 Ni COPRECIPITATION RATE

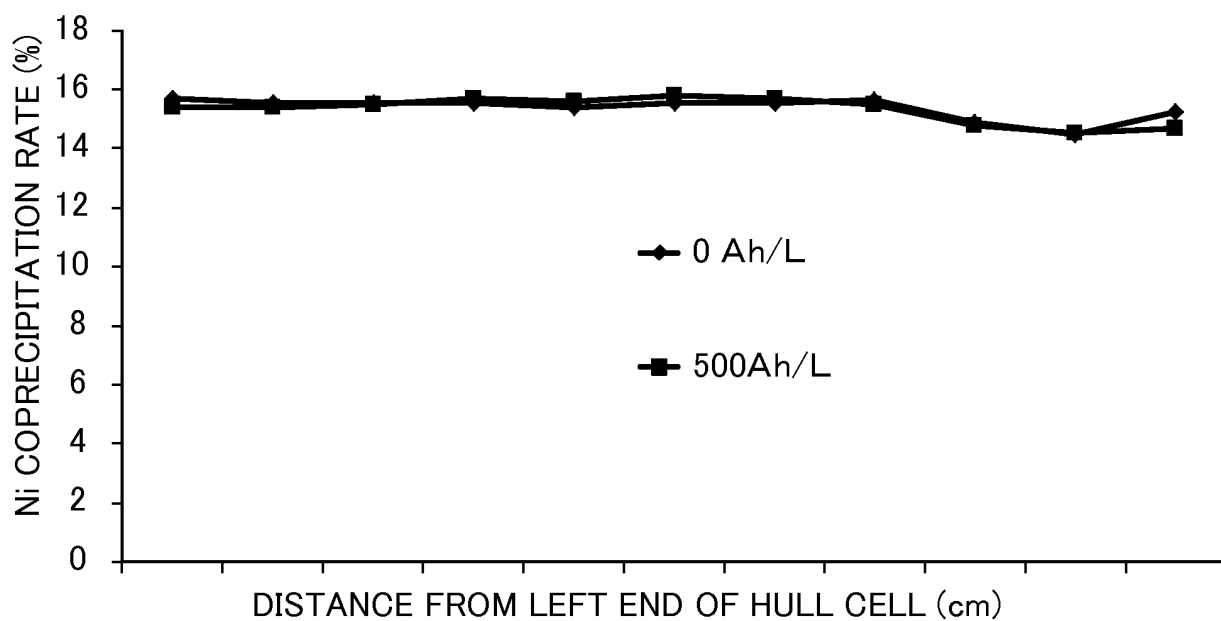


FIG.8

EXAMPLE 2 FILM THICKNESS DISTRIBUTION

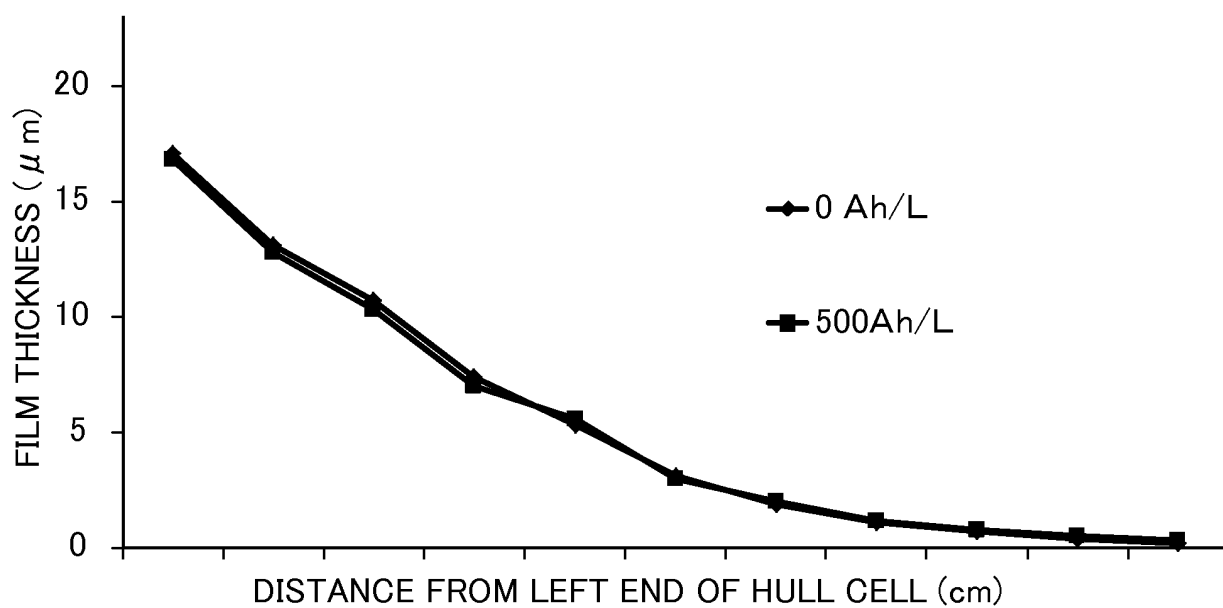


FIG.9

EXAMPLE 2 Ni COPRECIPITATION RATE

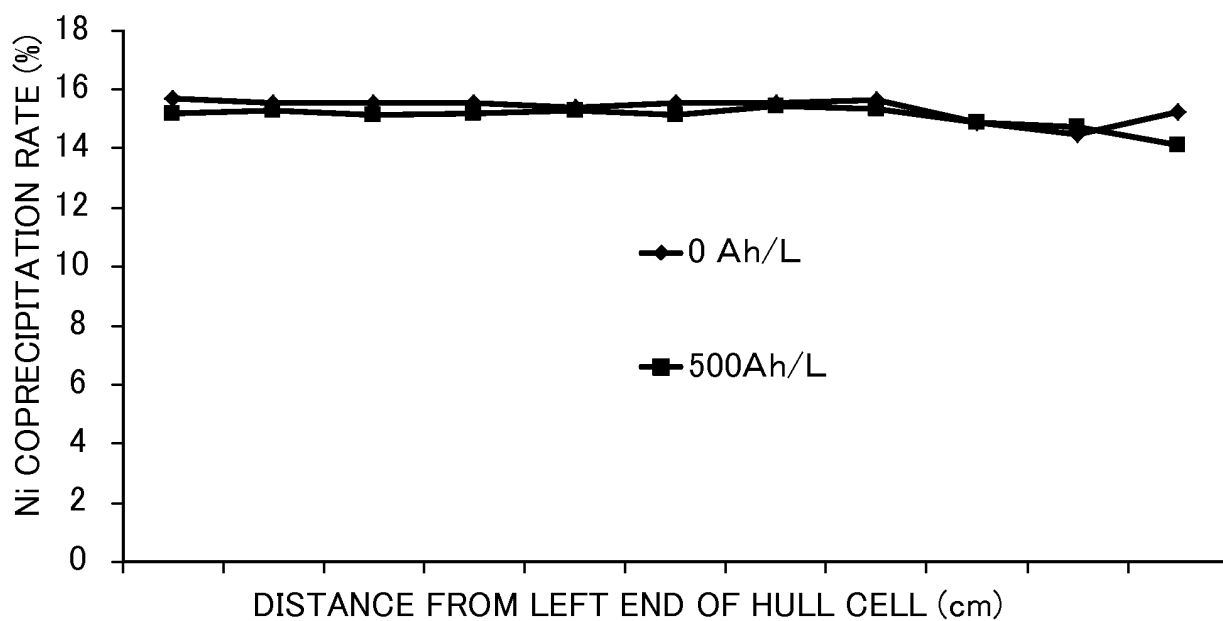


FIG.10

EXAMPLE 3 FILM THICKNESS DISTRIBUTION

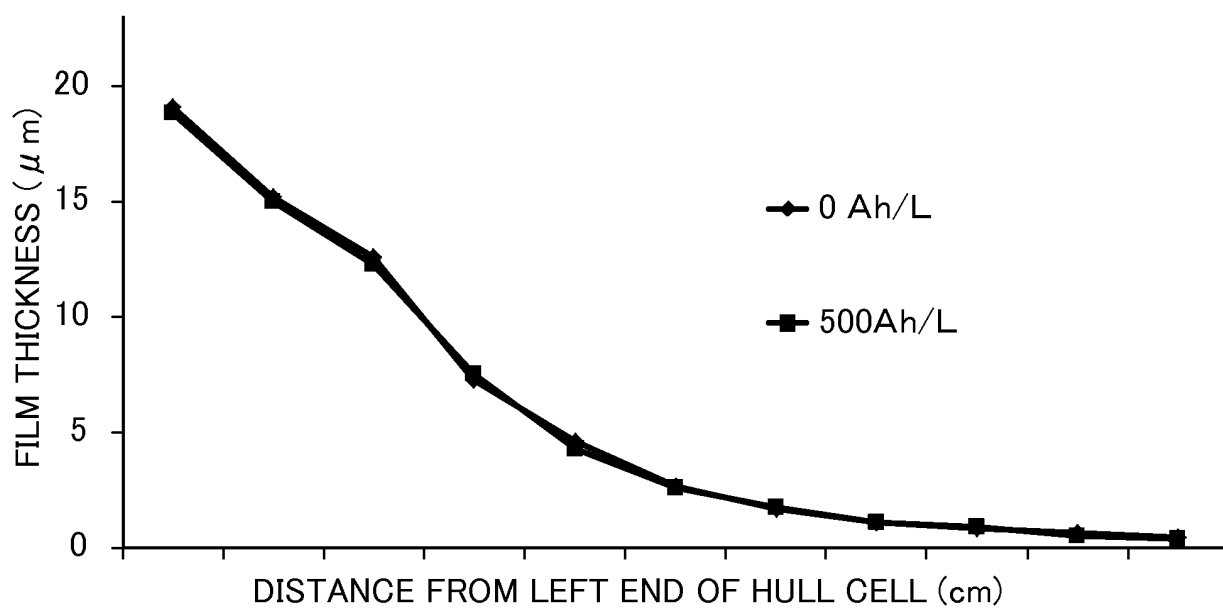


FIG.11

EXAMPLE 3 Ni COPRECIPITATION RATE

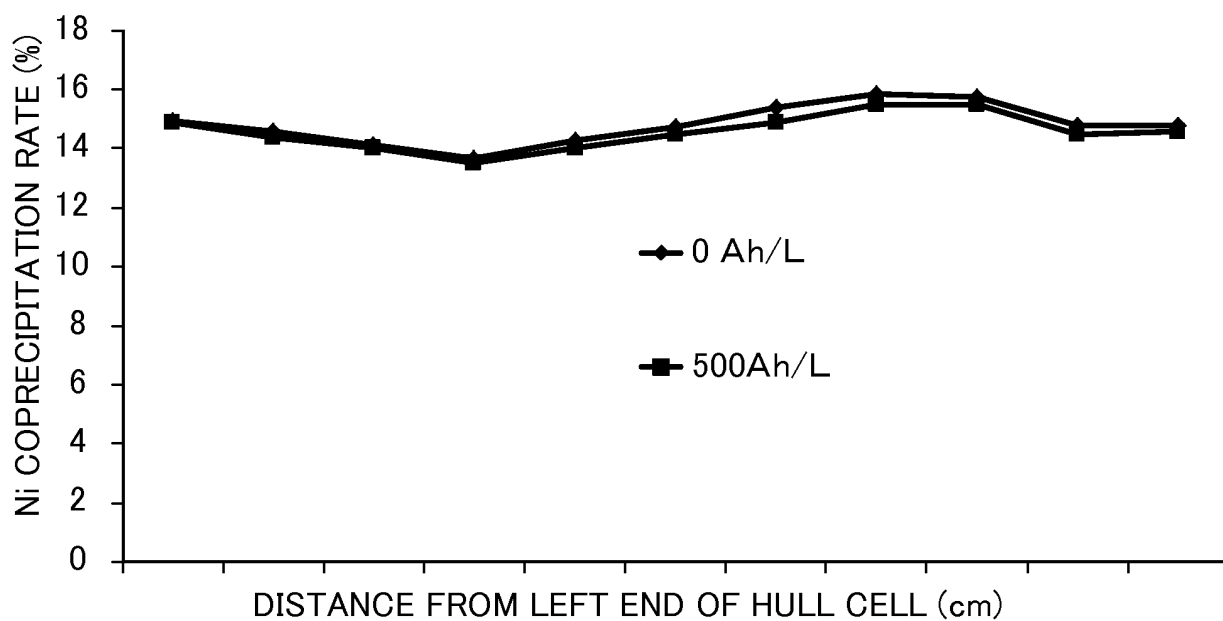


FIG.12

COMPARATIVE EXAMPLE 1 FILM THICKNESS DISTRIBUTION

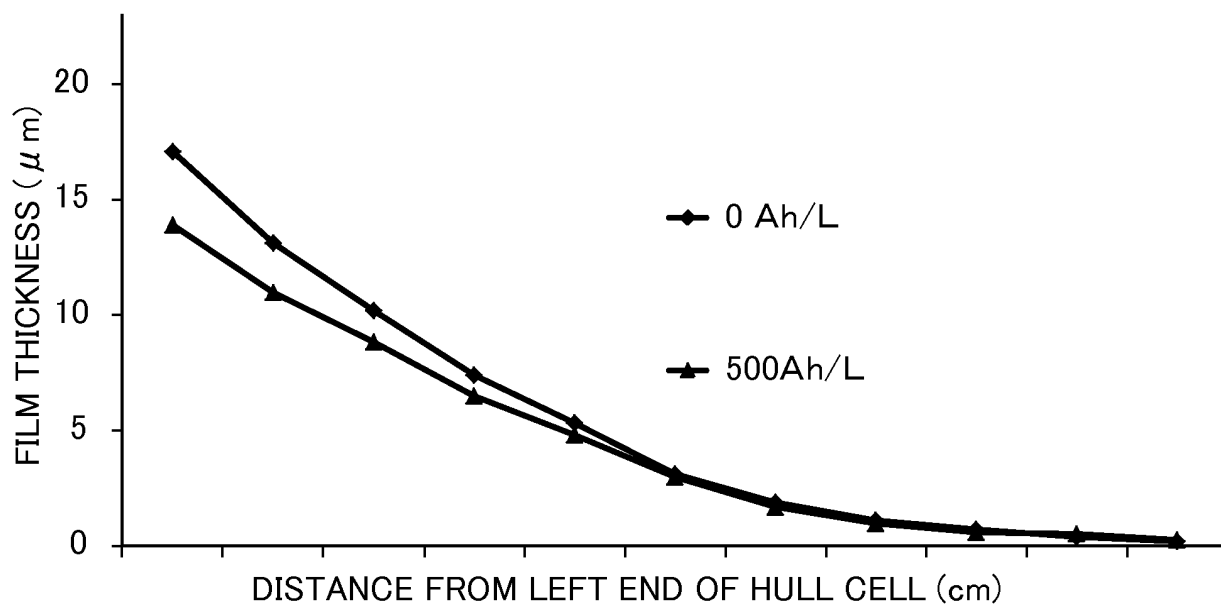


FIG.13

COMPARATIVE EXAMPLE 1 Ni COPRECIPITATION RATE

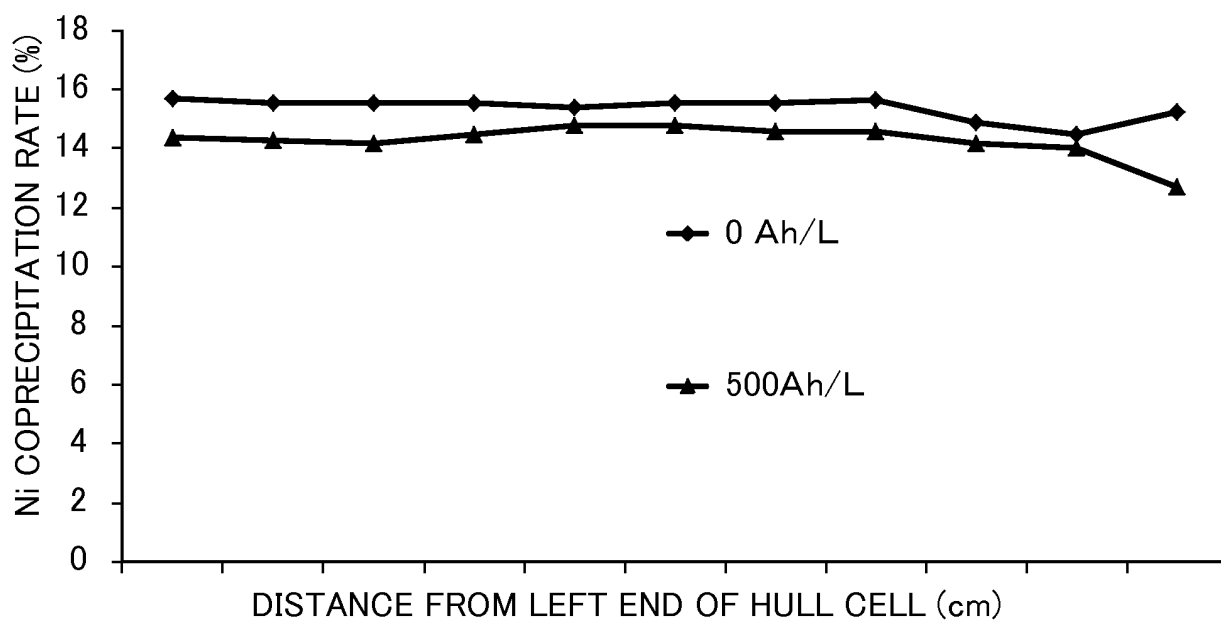


FIG.14

COMPARATIVE EXAMPLE 2 FILM THICKNESS DISTRIBUTION

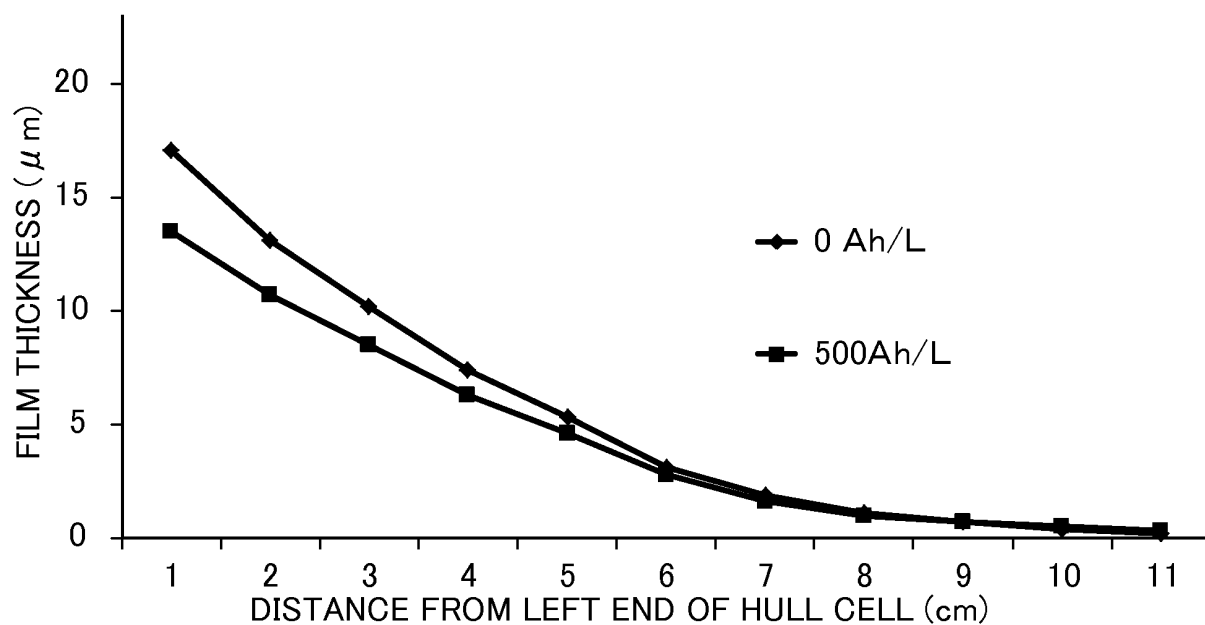
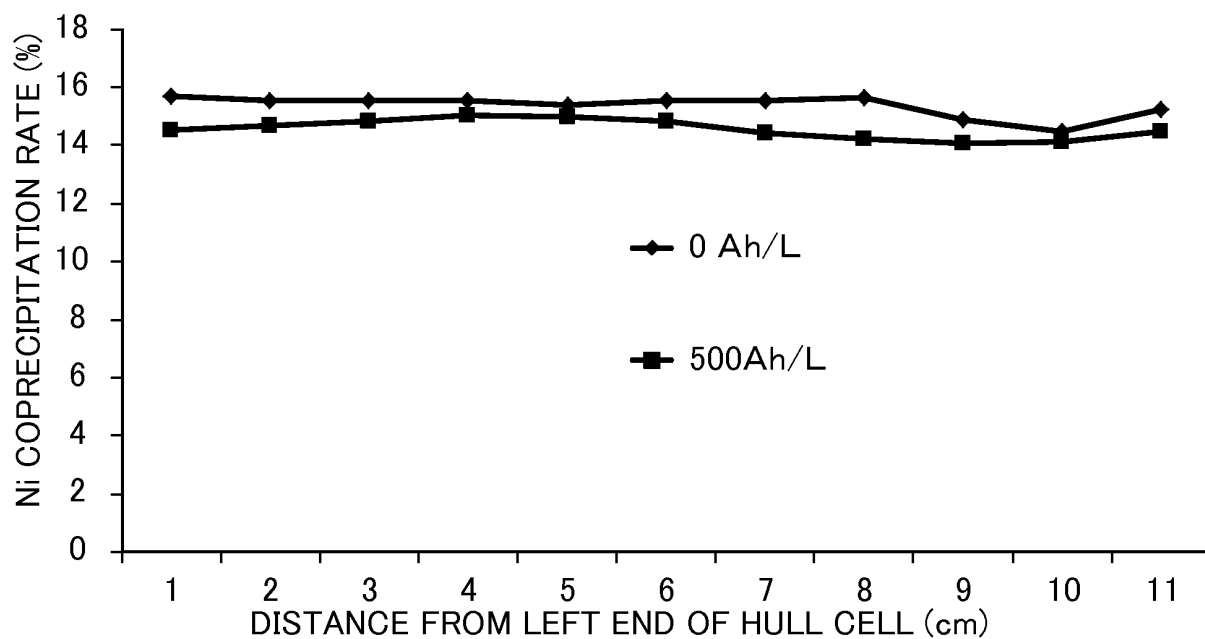


FIG.15

COMPARATIVE EXAMPLE 2 Ni COPRECIPITATION RATE



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2019/005548

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. C25B11/04 (2006.01) i, C25D3/22 (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)

Int. Cl. C25B11/04, C25D3/22

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 1971-2019

Registered utility model specifications of Japan 1996-2019

Published registered utility model applications of Japan 1994-2019

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.
Y	JP 1-298192 A (EBARA UDYLLITE KK) 01 December 1989, claims, examples (Family: none)	1-14
Y A	JP 2004-68153 A (NIPPON HYOMEN KAGAKU KK) 04 March 2004, paragraph [0010], examples (Family: none)	1-5, 8-12 6-7, 13-14
Y	JP 3-240987 A (TDK CORP.) 28 October 1991, page 3, lower left column, lines 1-6, examples (Family: none)	1-14
Y	JP 9-157879 A (TDK CORP.) 17 June 1997, claims, paragraphs [0007], [0008], [0014], [0035] (Family: none)	1-14

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

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Date of the actual completion of the international search
08.04.2019Date of mailing of the international search report
07.05.2019Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

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C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2000-256898 A (PERMELEC ELECTRODE LTD.) 19 September 2000, paragraph [0007], examples & US 6432293 B1, column 2, lines 40-47, examples	1-14
A	WO 2016/075963 A1 (DIPSOL CHEMICALS CO., LTD.) 19 May 2016, entire text & US 2017/0022621 A1, entire text & EP 3042985 A1 & CN 106550606 A	1-14
A	JP 2013-216958 A (MATEX JAPAN CO., LTD.) 24 October 2013 (Family: none)	1-14
A	JP 2006-503187 A (ELTECH SYSTEMS CORPORATION) 26 January 2006, entire text & US 2004/0031692 A1, entire text & US 6527939 B1 & WO 2004/038071 A2 & WO 2001/000905 A1 & EP 1552041 A1 & CA 2501229 A1 & KR 10-2005-0083767 A	1-14

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2002521572 W [0004]
- JP 2007002274 A [0005]
- WO 2016075963 A [0006]
- JP 2008539329 W [0007]