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(71) Applicant: **KAWASAKI STEEL CORPORATION**
1-28, Kitahonmachi-dori 1-Chome
Chuo-ku, Kobe-Shi Hyogo 651(JP)

(72) Inventor: **MATSUDA, Akira**
1351, Sonno-cho Chiba-shi
Chiba 281(JP)

(72) Inventor: **YOSHIHARA, Takahisa**
3-12, Nitona-cho Chiba-shi
Chiba 280(JP)

(72) Inventor: **KIMURA, Hajime**
1351, Sonno-cho Chiba-shi
Chiba 281(JP)

(74) Representative: **Henkel, Feiler, Hänzel & Partner**
Möhlstrasse 37
D-8000 München 80(DE)

(54) Zn-Ni ALLOY PLATING SOLUTION BASED ON CHLORIDE BATH.

(57) A Zn-Ni alloy electroplating solution for obtaining Zn-Ni alloy-electroplated steel with excellent surface appearance, which contains $ZnCl_2$ and $NiCl_2$ as major components. In the solution, the percentage molar concentration, x(%), of $Ni^{2+}/Ni^{2+} + Zn^{2+}$ and the concentration of chloride (at least one chloride selected from the group consisting of $AlCl_3$, NH_4AlCl_4, NH_cCl, KCl, NaCl, $CaCL_2$, $BaCl_2$, and $MgCl_2$), y (mol/liter), are kept within the following ranges:

$$-0.2x + 15.0 \geqq y \geqq -0.2x + 9.0$$

$$7.0 \geqq y \geqq 0.2$$

$$60 \geqq y \geqq 10$$

Croydon Printing Company Ltd

DESCRIPTION

TECHNICAL FIELD

This invention relates to Zn-Ni alloy electroplating solutions for use in plating steel sheets to form Zn-Ni alloy deposits having improved surface appearance.

BACKGROUND ART

It is well known in the art that Zn-Ni alloy plated steel sheets have improved surface properties such as corrosion resistance, weldability, and paintability, and that Zn-Ni alloy deposits consisting essentially of a gamma-phase and having a nickel content in the range from 10% to 20% by weight exhibit the best corrosion resistance.

Industrially feasible electroplating baths for Zn-Ni alloy plating are sulfate and chloride baths. The chloride bath has the advantages that liquid flow has less influence on the nickel content of deposits, that it can be operated at higher current density, and that power consumption is lower because of the increased electric conductivity of the solution than is the case with the sulfate bath, but the bath is difficult to form deposits having good appearance.

Making investigations to improve the appearance of Zn-Ni alloy deposits resulting from plating solutions based on zinc chloride $ZnCl_2$ and nickel chloride $NiCl_2$ in water, the inventors found that the appearance of Zn-Ni alloy deposits can be improved by adding at least one additional chloride selected from the group consisting of $AlCl_3$, NH_4AlCl_4, NH_4Cl, KCl, $CaCl_2$, $BaCl_2$, $NaCl$ and $MgCl_2$ to the solution in an amount of 0.2 mols per liter.

It was, however, found that when the above-described additional chlorides were added, there was the likelihood that the nickel content of deposits would increase and particularly at a high current density of 50 A/dm^2 or more, it would exceed the optimum range between 10% and 20% by weight.

DISCLOSURE OF INVENTION

Then the inventors continued investigations on the correlation between plating bath composition and alloy deposit composition in Zn-Ni alloy plating in order to produce Zn-Ni alloy deposits exhibiting improved appearance and having a nickel content within the above-defined optimum range. As a result, the inventors have found that the concentration of an additional chloride added should fall within a specific range in relation to the ratio of molar concentration between nickel and zinc.

Provided that the ratio of molar concentration between nickel and zinc is expressed as the molar concentration ratio of $Ni^{2+}/(Ni^{2+} + Zn^{2+})$, deposits tend to increase their nickel content substantially in proportion to this molar concentration ratio on one hand, and in proportion to the concentration of the additional chloride on the other hand. It has thus been found that the nickel content of deposits will consistently fall within the optimum range of 10% to 20% by weight when the concentration of the additional chloride is controlled within a proper range in relation to the molar concentration ratio of $Ni^{2+}/(Ni^{2+} + Zn^{2+})$.

According to the present invention, there is provided a Zn-Ni alloy electroplating solution, characterized in that the molar concentration ratio X expressed in percent of $Ni^{2+}/(Ni^{2+} + Zn^{2+})$ in the solution and the concentration Y expressed in mol/liter of an additional chloride added to the solution are controlled to fall within the range defined by the following equations:

$$\left.\begin{array}{r} -0.2X + 15.0 \geqq Y \geqq -0.2X + 9.0 \\ 7.0 \geqq Y \geqq 0.2 \\ 60 \geqq X \geqq 10 \end{array}\right\} (1)$$

In the practice of the present invention, the total concentration of nickel and zinc in the plating solution preferably ranges from 1 to 4 mols per liter of the solution. Total concentrations of nickel and zinc of lower than 1 mol/liter tend to form burnt deposits having unacceptable appearance. At total concentrations of higher than 4 mols/liter, there are increased drag-outs from the plating bath, undesirably increasing the cost. The plating solution is not particularly limited with respect to pH and temperature while it is practically at pH 1 to 6 and a temperature of 40° to 70°C.

The machanism by which the additional chloride in the plating solution has an influence on the nickel content of deposits is presumed as follows although the exact mechanism has not been well understood. Since the Zn-Ni alloy plating is codeposition of different metals, a barrier layer of zinc hydroxide $Zn(OH)_2$ formed at the cathode interface prevents nickel, which is otherwise readily depositable, from depositing so that even when the molar ratio of Zn to Ni is 1:1 in the bath, deposition of zinc preferentially takes place by way of the zinc hydroxide barrier layer. Nevertheless, if a chloride, for example, ammonium chloride NH_4Cl is present in the bath as in the present invention, the following two reactions:

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$$
$$NH_4^+ + OH^- \longrightarrow NH_4OH$$

simultaneously take place at the cathode interface, probably reducing the thickness of the zinc hydroxide barrier layer. Then, deposition of nickel is correspondingly facilitated so that deposits with increased nickel contents will form.

Similarly, the additional chloride in the plating bath has an influence on the appearance of Zn-Ni alloy deposits in the following way. There will be readily formed hydrated oxides and analogues on Zn-Ni alloy deposits in the presence of Cl^- ions, to which OH^- ions at the cathode interface contribute. If a chloride such as ammonium chloride NH_4Cl is present in the bath, OH^- ions are removed through the following reaction:

$$NH_4^+ + OH^- \longrightarrow NH_4OH$$

so that formation of colored hydrated oxides is precluded, resulting in aesthetic Zn-Ni alloy deposits having metallic gloss.

BRIEF DESCRIPTION OF DRAWING

Fig. 1 diagramatically shows how the nickel content of Zn-Ni alloy deposits varies with the concentration of ammonium chloride added to the plating solution at varying molar concentration ratios of $Ni^{2+}/(Ni^{2+} + Zn^{2+})$; and

Fig. 2 diagramatically shows the concentration of the chloride added vs. the molar concentration ratio of $Ni^{2+}/(Ni^{2+} + Zn^{2+})$, demonstrating their limits allowing the nickel content of Zn-Ni alloy deposits to fall within the optimum range.

BEST MODE FOR CARRYING OUT INVENTION

Examples of the Zn-Ni alloy electroplating solution according to the present invention are given below by way of illustration.

Example 1

Plating baths were prepared by adding ammonium chloride NH_4Cl in amounts varying from 0 to 7.0 mols/liter (0 to 375 g/liter) to a solution containing 136 g/liter (1 mol/liter) of zinc chloride $ZnCl_2$ and 238 g/liter (1 mol/liter) of nickel chloride hexahydrate $NiCl_2 \cdot 6H_2O$ and having a molar concentration of Ni^{2+} adjusted to 50%. Using these plating baths, electroplating was carried out at a current density of 75 A/dm^2 so that the built-up of Zn-Ni alloy deposited might be 20 g/m^2.

The resulting deposits were determined for gloss and nickel content. The gloss and nickel content for each amount of ammonium chloride added are shown in Table 1. The data of Table 1 reveal that colored deposits having poor appearance are formed in the absence of ammonium chloride, but the gloss and appearance of deposits are improved when ammonium chloride is added in amounts of 0.2 mols/liter or more. On the other hand, it is evident that the nickel content of deposits increases with the increasing amounts of ammonium chloride added and goes beyond the optimum range of 10% to 20% by weight when the amount of ammonium chloride exceeds 5 mols/liter.

It should be noted that the gloss is expressed in the Gs(60) value according to JIS Z 8741, and the appearance is evaluated using the following criterion:

O: metallic gloss, untarnished, uniform
Δ: somewhat tarnished or nonuniform
X: tarnished

Example 2

Plating baths were prepared by adding ammonium chloride (NH_4Cl) in amounts varying from 0.2 to 7.0 mols/liter to solutions containing varying percentage molar concentrations of zinc chloride $ZnCl_2$ and nickel chloride hexahydrate $NiCl_2 \cdot 6H_2O$. Using these baths, electroplating was effected at a current density of 75 A/dm^2 so that the build-up of Zn-Ni alloy deposited might be 20 g/m^2.

Fig. 1 shows the nickel content of deposits plotted relative to the concentration of ammonium chloride added for different molar concentration ratios of $Ni^{2+}/(Ni^{2+} + Zn^{2+})$.

The resulting alloy deposits all appeared aesthetically good, but the nickel content increased as the concentration of ammonium chloride added is increased, indicating that the concentration of ammonium chloride should fall within a proper range depending on the molar concentration ratio of $Ni^{2+}/(Ni^{2+} + Zn^{2+})$. This is more clearly shown in Fig. 2 where X axis represents the molar concentration ratio of $Ni^{2+}/(Ni^{2+} + Zn^{2+})$ as expressed in percent and Y axis represents the concentration of the chloride as expressed in mol/liter. Fig. 2 demonstrates that the optimum range is defined by the following three equations:

$$-0.2X + 15.0 \geqq Y \geqq -0.2X + 9.0$$

$$7.0 \geqq Y \geqq 0.2$$

$$60 \geqq X \geqq 10$$

It should be noted that the upper limit of 7.0 mols/liter was imposed on the concentration of the chloride in this example because it is the saturation level.

Example 3

Using plating baths containing various chlorides, a Zn-Ni alloy was deposited on a steel sheet to a build-up of 20 g/m^2. The gloss, appearance, and nickel content of the resulting deposit for each bath composition were shown in Table 2. Run Nos. 1 to 10 and comparative run Nos. 11 and 12 in Table 2 are also plotted in Fig. 2 with the same numerical designation. In all of run Nos. 1 to 10, the deposits exhibited high gloss and satisfactory appearance and their nickel contents fell in the optimum range depicted as a cross-hatched region in Fig. 2.

As evident from these data, by using the chloride bath of the present invention, Zn-Ni alloy deposits can be readily and consistently formed having improved corrosion resistance, aesthetic appearance and a nickel content within the optimum range between 10% and 20% by weight.

Table 1

Run No.	Amount of NH_4Cl added (mol/ℓ)	Gloss (%)	Appearance	Nickel content (%)	Remarks
1	-	9.2	X	11.0	Comparison
2	0.05	14.5	X	11.3	Comparison
3	0.1	27.6	Δ	11.5	Comparison
4	0.2	50.3	O	12.0	Invention
5	1.0	80.5	O	12.8	Invention
6	3.0	127.6	O	16.4	Invention
7	5.0	151.6	O	19.8	Invention
8	7.0	83.2	O	24.2	Comparison

Table 2

Run No.	$ZnCl_2$ Concentration (mol/ℓ)	$NiCl_2$ $6H_2O$ concentration (mol/ℓ)	$\frac{Ni^{2+}}{Ni^{2+} + Zn^{2+}}$ (%)	Chloride		Current density (A/dm^2)	Gloss (%)	Appearance	Ni content of deposit (%)	Remarks
				Type	Amount (mol/ℓ)					
1	1.0	0.5	33	NH_4Cl	5.0	50	76.5	O	14.8	Invention
2	1.5	1.5	50	KCl	2.0	100	106.8	o	14.6	"
3	2.4	0.6	20	$AlCl_3$	5.5	75	68.5	O	10.8	"
4	1.2	0.8	40	NH_4AlCl_4	6.0	25	78.6	O	17.8	"
5	1.2	1.8	60	NaCl	1.5	90	120.4	O	16.5	"
6	0.8	0.8	50	$CaCl_2$	4.0	75	88.4	O	18.2	"
7	1.1	0.9	45	$BaCl_2$	0.5	60	62.3	O	10.6	"
8	1.8	1.2	40	$MgCl_2$	3.0	150	111.6	O	13.0	"
9	1.5	0.5	25	NH_4Cl KCl	4.0 2.5	100	72.3	O	14.5	"
10	1.4	0.6	30	NaCl $CaCl_2$ $BaCl_2$	2.0 1.0 1.0	50	91.2	O	11.5	"
11	1.0	1.0	50	KCl	6.0	75	66.7	O	21.8	Comparison
12	1.2	0.3	20	NaCl	2.0	50	56.2	O	5.2	"
13	1.0	0.8 $NiSO_4 \cdot 7H_2O$ 0.2	50	NH_4Cl	3.0	100	90.2	O	12.8	Invention

CLAIM

1. A Zn-Ni alloy electroplating solution based on zinc chloride and nickel chloride, characterized in that the molar concentration ratio X expressed in percent of $Ni^{2+}/(Ni^{2+} + Zn^{2+})$ in the solution and the concentration Y expressed in mol/liter of an additional chloride added to the solution are controlled to fall within the range defined by the following equations:

$$-0.2X + 15.0 \geqq Y \geqq -0.2X + 9.0$$

$$7.0 \geqq Y \geqq 0.2$$

$$60 \geqq X \geqq 10$$

2. The Zn-Ni alloy electroplating solution according to claim 1 wherein the additional chloride is at least one selected from the group consisting of $AlCl_3$, NH_4AlCl_4, NH_4Cl, KCl, $CaCl_2$, $BaCl_2$, NaCl, and $MgCl_2$.

FIG.1

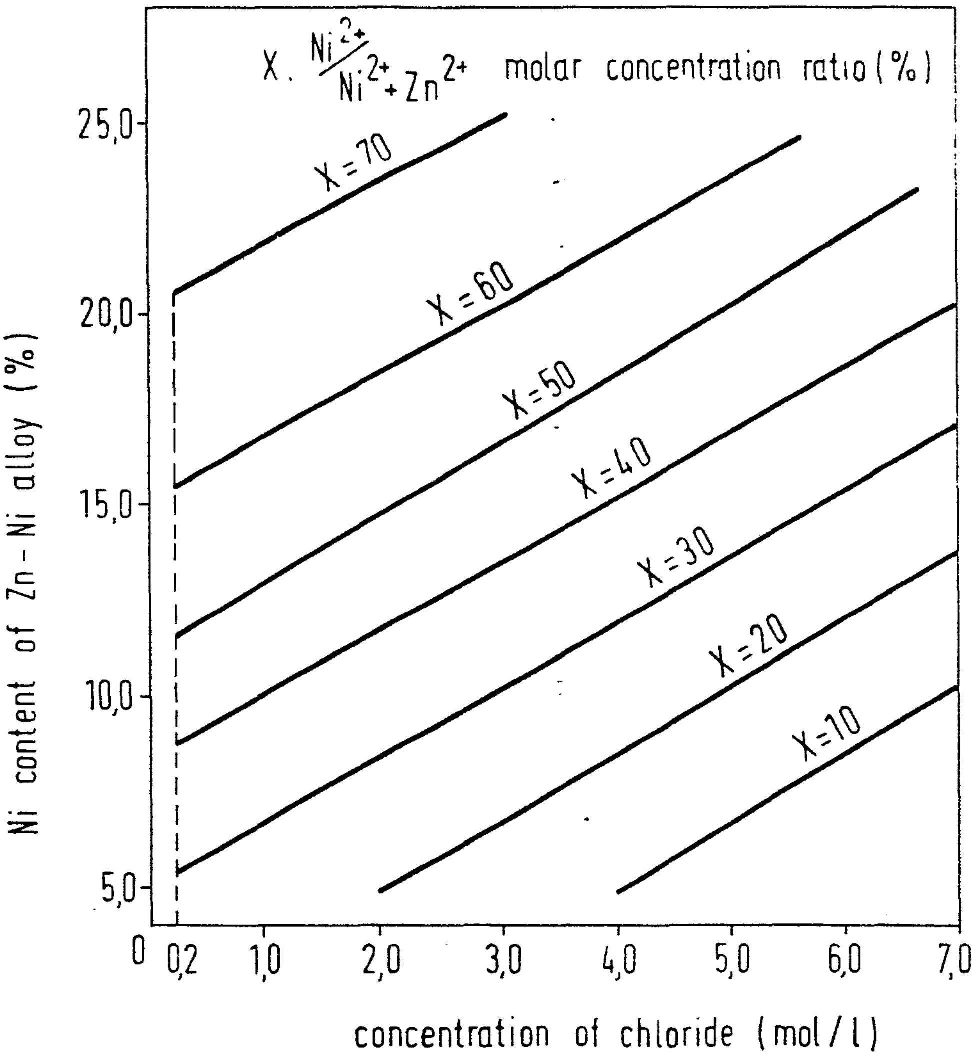
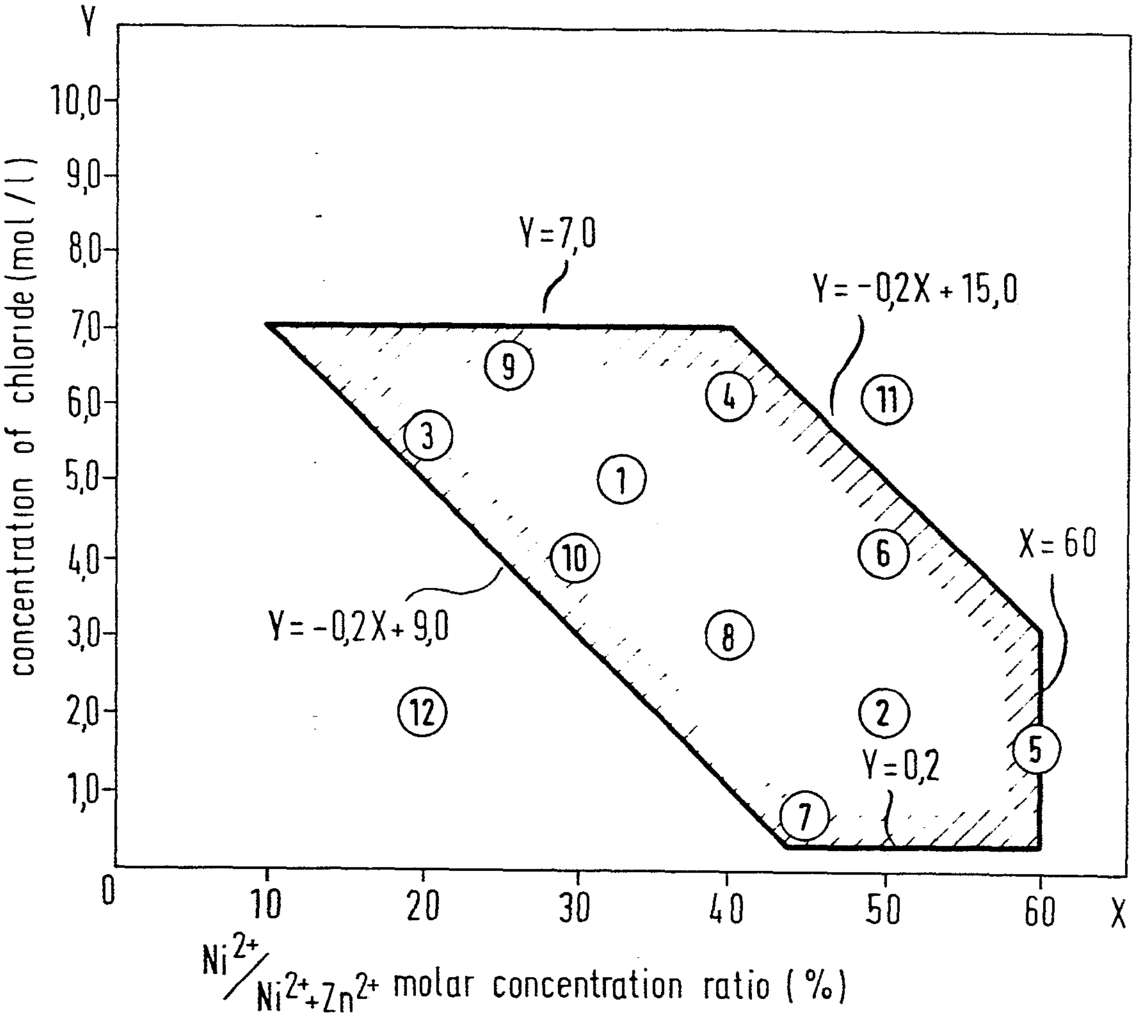

X. $\frac{Ni^{2+}}{Ni^{2+}+Zn^{2+}}$ molar concentration ratio (%)
X=70
X=60
X=50
X=40
X=30
X=20
X=10
25,0
20,0
15,0
10,0
5,0
0
0,2
1,0
2,0
3,0
4,0
5,0
6,0
7,0
Ni content of Zn-Ni alloy (%)
concentration of chloride (mol/l)

FIG. 2


Y
10,0
9,0
8,0
7,0
6,0
5,0
4,0
3,0
2,0
1,0
0
concentration of chloride (mol / l)
Y=7,0
Y=-0,2X+15,0
Y=-0,2X+9,0
X=60
Y=0,2
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫
10
20
30
40
50
60
X
Ni2+/Ni2++Zn2+ molar concentration ratio (%)

INTERNATIONAL SEARCH REPORT

0147463

International Application No. PCT/JP83/00196

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl^3 C25D3/56

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC	C25D3/56

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category*	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	JP, A, 58-55585 (Kawasaki Steel Corp.) 01. April. 1983 (01.04.83) Column of Claim	1, 2

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] September 1, 1983 (01.09.83)	Date of Mailing of this International Search Report [2] September 12, 1983 (12.09.83)
International Searching Authority [1] Japanese Patent Office	Signature of Authorized Officer [20]

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