Studies on the Electrodeposition of Ternary Alloys of Iron, Nickel, and Chromium from a Chloride Bath

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Electrodeposition of iron, nickel, and chromium ternary alloys was investigated. The bath was constituted of chlorides of the respective elements and ammonium chloride. For the cathode, copper, iron, nickel, and chromium plate were used. For the anode, a relatively large platinum plate was used. The optimum plating conditions were determined to be: bath composition of 0.5 M/l CrCl_3 , 0.1~0.2 M/l FeCl_2 , 0.1~0.3 M/l NiCl_2 , and 200 g/l NH_4Cl , pH value of 2.0, cathodic current density of 10~30 A/dm² and bath temperature of 20~30 °C. Under the above conditions deposits have the composition of 7~25 wt.% Cr and 5~30 wt.% Ni, and have a fine metallic lustre. However, the deposits began to exhibit microscopic cracks when they exceeded 10~15 μ in thickness. Cathodic current efficiency was maintained in the range of 30~40% under the above conditions.

These alloy depositions seem to be "regular codeposition" characterized by the diffusion control of iron and nickel ions. It is considered that the high concentration of chlorides caused the chromic ion to stay mainly in the form of mono- or dichloroquo complex ions which possess a green color, and that these green species were more feasible than the violet hexaquo complex ion to discharge on the cathode.

1. Introduction

Some investigators^{1),2)} have reported on the electrodeposition of iron-chromium alloys. However, only a few papers^{3),4)} have been published about the electrodeposition of iron, chromium and nickel ternary alloys. Machu and his co-workers⁶⁾ have studied the electrodeposition from a sulphate bath to which a considerable amount of urea was added, and Kalyuzhunaya and his co-workers⁵⁾ also conducted studies on the

same bath to which sodium fluoride and sodium citrate were added. The methods described in these two reports have been reproduced in our laboratory, and it was observed that the method of Kalyuzhunaya et al was excellent in respect to the deposition appearance and current efficiency, but was otherwise inferior to Machus' method because of the difficulty of maintaining the optimal plating conditions.

Owing to the difficulty of the chromium deposition, one must consider the conditions

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under which a good deposition of chromium is achieved. Generally speaking, the deposition of chromium is carried out at high current densities, while on the contrary, metals of the iron group are plated at relatively low current densities. To minimize the difficulty arising from the above two contradictory requirements, a chloride bath in which iron group metals are plated at relatively high current densities seems to be more adequate than the sulphate bath. A chloride bath has also several other advantages, that is, a high electrical conductivity and a high efficiency of the anodic dissolution. For these reasons, a chloride bath was selected for the ternary alloy deposition in the experiments described in this paper.

2. Experimental

Reagents Chemically pure grade of chromium trichloride, nickel chloride, ferrous chloride and ammonium chloride were used. The green form of chromium trichloride was selected.

Electrodes For the cathode, copper discs were used which were 10mm. in diameter and 1 mm thick, and had a conduction stem 1mm wide and 40 mm long, which was coated with epoxyresin for insulation. Prior to the deposition, the cathode was polished by emery paper No. 0 ~ 3, followed by washing with alkaline and acidic solutions. For the anode, a relatively large platinum plate was used. To avoid any considerable change in the pH and concentration, as much as 200 cc of the electrolyte were used, which were discarded after three or four runs.

Electrolytic cell The cell used is shown in Fig. 1. It consists of anodic and cathodic compartments, and is intended to give a uniform electric field on the both sides of the cathode. The two compartments are separated by a long electrolyte path and a cock valve packed with glass wool. Stirring of the solution was omitted, for

1: anode compartment, 2: platinum anode,
3: cathode compartment, 4: cathode,
5: glass wool

Fig. 1 Electrolytic Cell

good deposits could not be obtained under stirring.

The method of analysis of the deposits After electrodeposition, the epoxyresin coating was removed from the cathode stem, the cathode was dried at 120°C for an hour, and weighed. The deposits were dissolved away in 2 cc of phosphoric acid, the discs washed with water, and dried again at 120°C. Then, the copper discs were weighed once more. The difference in weight was regarded as the weight of the deposit, as copper does not dissolve in phosphoric acid. Two or three cc of a mixture of concentrated nitric and sulphuric acids were added to the solution in which the deposits had been dissolved, and the solution was heated till white fumes appeared. Then, chromium in this solution was oxidized to chromate by ammonium persulphate and reduced to chromic ion by adding an excess of ferrous sulphate. Chromium was determined by back titration with potassium permanganate. Nickel was also determined by a gravimetric

method through nickel dimethylglyoxime. The weight of iron was calculated by subtracting the sum of chromium and nickel from the total weight of the deposits.

Calculation of the current efficiency and the thickness of the deposits If η_{Fe} , η_{Ni} , η_{Cr} are designated to be the current efficiencies of the iron, nickel and chromium depositions respectively, they are calculated by the following equations, $\eta_{Fe} = W_{Fe} \cdot 3456 / i \cdot t$, $\eta_{Ni} = W_{Ni} \cdot 3287 / i \cdot t$, $\eta_{Cr} = W_{Cr} \cdot 5568 / i \cdot t$ (%), where, W_j is the weight of species j in gram. i refers to the electrolyzing current in ampere, and t is the deposition time in sec. The thickness of the electrodeposited layer (d) is calculated by the following equation, $d = (W_{Fe} / 7.87 + W_{Cr} / 7.19 + W_{Ni} / 8.90) 10^4 / (\text{cathode area, cm}^2) (\mu)$.

3. Results

The influence of the composition of the electrolyte on that of the deposits To examine the characteristics of the plain chromium deposition, plating was performed with

the bath containing chromium trichloride in various concentrations. It was presumed from the results of preliminary experiments, that no deposits could be obtained under the ordinary plating conditions from a bath containing less than 0.3 M/l of chromium trichloride, and that the addition of ammonium chloride up to saturation greatly improved the deposition. Other chlorides such as those of alkali and alkali-earth metals, were also used for the ternary alloy deposition; however, all of them proved worse than ammonium chloride, as shown in Table 1, either in respect to current efficiency or to appearance.

In Fig. 2, current efficiencies are plotted against current densities. It is clearly seen that the higher the concentration of chromium chloride the lower the current efficiency, and the current density at which good efficiencies are obtained is raised as the temperature increases. From these experiments, chromium trichloride concentration was fixed at 0.5 M/l hereafter.

Table 1 The Effects of Addition of Various Chlorides

Bath composition; $CrCl_3$ 0.5M/l, $FeCl_2$ 0.15M/l, $NiCl_2$ 0.15M/l
temperature; 30°C, pH; 2.0, current density; 20 A./dm².
deposition time; 5 min.

Kind of added chloride	Conc. (g/l)	Composition of alloy (%)			Thickness (μ)	Current efficiency (%)	Surface appearance
		Fe	Cr	Ni			
Reference	0	75.3	9.3	15.4	3.0	13.9	grey, with colloidal film
NH_4Cl	50	75.1	10.1	14.8	3.9	18.6	grey, dark spots
	100	78.1	11.8	10.1	5.3	25.1	metallic
	200	78.8	12.2	9.0	7.7	37.6	metallic, bright
	satd.	79.0	12.4	8.6	7.6	36.2	metallic, bright
$CaCl_2$	50	75.9	5.5	18.6	1.7	8.0	metallic, bright
	100	77.7	11.2	11.1	3.9	18.4	grey, dark spots
	200	80.0	10.1	9.7	4.3	20.2	grey, dark spots
$MgCl_2$	50	78.4	8.3	13.3	1.2	5.8	metallic, bright
	150	73.7	9.8	16.5	3.3	15.4	dark grey
LiCl	50	77.7	10.4	11.9	2.7	12.7	metallic, bright
	150	78.0	12.5	9.5	4.4	21.3	mat
NaCl	50	92.7	0	7.3	0.6	3.0	mat (but flat)
	150	91.8	0	8.2	0.9	4.0	mat (but flat)

Temperature; $\square$ —20°C, $\circ$ —40°C, $\triangle$ —60°C.

Fig. 2 The dependences of the current efficiencies on the current densities in plain chromium deposition from a bath containing 200 g/l NH_4Cl and 0.5 M/l CrCl_3 in Fig. 2a, 1.0 M/l CrCl_3 in Fig. 2b and 1.5 M/l CrCl_3 in Fig. 2c.

The effects of the concentrations of iron (II) and nickel chlorides on the composition of the deposits

In Fig. 3, the composition of the deposits is shown together with current efficiency against the current density. Bath composition was iron (II) 0.2 M/l, and nickel 0.1 M/l. From Fig. 3, it is found that the tendency of nickel to deposit is so minute relative to that of iron, that nickel does not deposit virtually at high current densities. On the other hand, chromium content of the deposits increases as the current density is raised. From the current efficiency curves, it is seen that the current efficiency is above 30% over the whole range of current densities used. To avoid the diminution of the nickel content of the deposit at high current densities, nickel

Fig. 3b The same as Fig. 3a, except for the temperature of bath 60°C.

Bath composition; CrCl_3 0.5 M/l, FeCl_2 0.2 M/l, NiCl_2 0.1 M/l, NH_4Cl 200 g/l, temperature; 20°C, pH 2.0, deposition time; 5 min. The numbers over respective curves denote total deposit, iron, chromium and nickel respectively.

Fig. 3a The dependences of the deposit compositions and current efficiencies on the current densities.

Bath composition; CrCl_3 0.5 M/l, FeCl_2 0.15 M/l, NiCl_2 0.15 M/l, NH_4Cl 200 g/l, temperature; 30°C , pH 2.0, deposition time; 5 min. The numbers over the respective curves have the same meanings as in Fig. 3a.

Fig. 4 The dependences of the deposit composition and the current efficiencies on the current densities.

to iron ratio in the bath composition was raised to yield the results shown in Figs. 4 and 5. The nickel contents of the deposits at high current densities are improved and the stable zone of deposit compositions is somewhat spread out in the range of 20 to 40 A/dm^2 in Fig. 5. The surface appearance after deposition is satisfactorily glossy at the range of low to medium current densities such as 10 to 20 A/dm^2 in Figs. 3a and 3b, but at higher current densities the deposits obtained are mat.

The influence of temperature The temperature effects at the current density of 20 A/dm^2 are shown in Figs. 6 and 7. As expected from the trend of nickel and plain chromium depositions, the higher the temperature the more difficult the chromium deposition, and the easier the nickel deposition are as is especially clear in Fig. 7.

Fig. 5 The same as Fig. 4, except for the bath composition: FeCl_2 0.1 M/l, NiCl_2 0.3 M/l.

Bath composition; CrCl_3 0.5 M/l, FeCl_2 0.15 M/l, NiCl_2 0.15 M/l, NH_4Cl 200 g/l, pH 2.0, current density; 20 A/dm^2 , deposition time; 5 min.

Fig. 6 The temperature dependence of the deposit compositions and the current efficiencies.

Fig. 7 The same as Fig. 6, except for the composition of bath; FeCl_2 0.1 M/l, NiCl_2 0.3 M/l.

Bath composition; CrCl_3 0.5 M/l, FeCl_2 0.1 M/l, NiCl_2 0.3 M/l, NH_4Cl 200 g./l. temperature; 30°C, current density; 20 A/dm², deposition time; 5 min.

Fig. 9 Effects of pH on the composition of deposits and current efficiency.

Bath composition; CrCl_3 0.5 M/l, FeCl_2 0.15 M/l, NiCl_2 0.15 M/l, NH_4Cl 200 g./l. temperature; 30°C, current density; 20 A/dm², deposition time; 5 min.

Fig. 8 Effects of pH on the composition of deposits and current efficiency.

The temperature dependence of the current efficiency is also shown in Figs. 6 and 7, and it can be seen that the total current efficiency is roughly parallel to that of the nickel deposition.

The effect of pH In Figs. 8 and 9, current efficiency and alloy compositions are plotted against various pH values of the bath. To adjust pH, hydrochloric acid and ammonia water were used. The most favourable values of pH are near 2.0, and above which the current efficiency decreases gradually. Above pH 3.0 some colloidal white film was formed on the cathode surface. Alloy composition varies when pH increases above 2.0, and increase in nickel and decrease in chromium are resulted.

The effects of deposition time Two problems are expected to arise during the deposition, that is, the variation of the

alloy composition and the decrease in the current efficiency with time. From Table 2, it is found that the variation of the alloy composition can be regarded as a negligible one, but the decrease in the current efficiency with the deposition time becomes evident after 10 min of operation. The rates of thickening of the deposit layers are roughly estimated to be $1 \sim 1.5 \mu/\text{min}$ or so at 20 A/dm^2 .

Microscopic state of the deposited surface

Up to a deposit thickness of 10μ under the same conditions as in Fig. 9, the surface appears to be flat and a continuous one. However, from $10 \sim 15 \mu$ (Photo. 1 and 2), some cracks start growing microscopically, in spite of the fact that the surfaces look unchanged to the naked eye. A sectional micrograph is also shown (Photo. 3). These sequences have also been pointed out in previous reports, and attributed to the inclusions of minute amounts of oxides.

The effects of the base metals Metals other than copper, that is, wrought iron, high carbon steel, and nickel and chromium plated copper were examined as the base metals in respect to their adhesion properties and surface appearance after the ternary alloy deposition. The wrought iron plate and the high carbon steel bar were pretreated by the same method as the discs described previously, while nickel and chromium were plated on copper from Watt's bath and a chromic acid bath respectively, then washed with water, and placed in the triple alloy plating bath without drying. On nickel, the adhesion and appearance were as good as on copper, while on iron and steel much more cracks were found to occur than on copper. In the case of chromium plated copper, although the adhesion of the deposited layer to the chromium layer was fairly good, adhesion between the copper base and the two deposited layers was so bad that the upper two layers began to peel off as the deposition proceeded.

Miscellaneous X-ray diagrams of the

Photo. 1

Photo. 2

Photo. 3

Photo. 1,2 Microscopic photograph of deposit surfaces. Plating conditions are the same as those of Table 2A. Thickness of deposit layer; 1: 24.5μ , 2: 7.7μ .
Photo. 3 Sectional photograph of a deposit 17.2μ of thickness.

deposits before heat treatment were compared with those obtained after heat treatment at 1000°C for an hour. For the sample before heat treatment, diffuse peaks which corresponded roughly to those of the respective

Table 2 Effects of Deposition Time

Temperature; 30°C, pH 2.0, current density; 20 A/dm²
 bath composition; CrCl₃ 0.5 M/l, NH₄Cl 200 g/l, FeCl₂ 0.15M/l(A),
 0.1 M/l (B), NiCl₂ 0.15 M/l (A), 0.3 M/l (B).

A								
Deposition time (min.)	Composition of deposits (wt.%)			Current efficiency (%)				Thick-ness (μ)
	Fe	Cr	Ni	Fe	Cr	Ni	total	
2	78.5	12.0	9.5	28.3	6.9	3.4	38.6	3.2
5	78.8	12.2	9.0	27.7	6.9	3.0	37.6	7.7
10	78.6	12.5	8.9	26.0	6.6	2.8	35.4	14.5
20	77.9	13.3	8.8	22.6	6.2	2.4	31.2	25.6

B								
Deposition time (min.)	Composition of deposits (wt.%)			Current efficiency (%)				Thick-ness (μ)
	Fe	Cr	Ni	Fe	Cr	Ni	total	
2	73.2	13.0	13.8	22.8	6.4	4.0	33.2	2.7
5	73.0	13.1	13.9	22.8	6.6	4.1	33.5	6.8
10	73.2	12.4	14.4	21.6	5.9	4.0	31.5	13.0
20	72.2	12.9	14.9	18.8	5.4	3.6	27.8	22.8

component metals were seen. These changed into sharper peaks by heat treatment and quenching. These peaks seem to correspond to the superposition of the two compounds, that is, CHI-Fe-Ni-Cr alloys and σ Fe-Cr alloys. Although these results indicated that the heat treatment was not performed satisfactorily, the treated deposits proved several times better than the untreated ones in the corrosion tests, which were carried out with solutions of 5% hydrochloric acid, 5% sulphuric acid and 20% sodium chloride.

4. Discussion

The ternary alloy deposition in this experiment is regarded as, what is called a "regular alloy plating system"⁷⁾ controlled by the diffusion of iron(II) and nickel ions. This is induced from the fact that the concentration of chromium (III) ion in the bath is quite high compared to those of iron (II) and nickel that the iron and nickel contents of the deposits decrease with the increase in the current density, and that on the con-

trary, they increase with rising temperature.

The chromium (III) complex ions such as $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ (green), $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ (green), and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (violet) may exist in a chloride bath. As the bath used in our experiments was always maintained green, either one or both of the former two complex ions were supposed to be present. It is likely thought that some of the water molecules coordinated to the chromic ion may be substituted by ammonia due to the high concentration of ammonium chloride in the bath; however, this substitution may be negligible at low pH range as existed in the present paper. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion is apparently easier to migrate to the cathode surface and discharge; however the fact, that ternary alloy deposition from a chloride bath of the violet type can be only performed with considerable difficulties as had been observed in preliminary experiments, may be attributed to the lower energy of the step change from $[\text{Cr}(\text{H}_2\text{O})_x\text{Cl}_{6-x}]^{(x-3)+}$ ($x=4$ or 5) to chromic adion, compared with that from the hexaquo chromic ion. In an acidic solution, some investigators⁸⁾ have reported about the re-

duction of chromic ion to chromous ion, but it has not been known whether chromium deposition from the chromic ion takes place through a path via chromous step or not. At any rate, the green type of chromic ion may be reduced to chromium metal easier than the violet type.

Some previous reports have emphasized the necessity of the coexistence of chromous or chromate ions for the deposition of chromium from its tervalent ion. In this experiment, chromate ion, if it existed in the solution, would be immediately reduced to tervalent by the ferrous ion present, and thus the catholyte can be regarded as containing no chromate ions. Nevertheless, the fact that the deposits were obtained satisfactorily indicates that the coexistence of the chromate ion is not a necessary condition. On the other hand, it seems plausible that the existence of chromous ion formed from the tervalent ion in the diffusion layer is necessary for the chromium deposition, because of the fact that the deposits could not be obtained satisfactorily under stirring. However, the existence of chromous ion may not be a necessary condition of chromium deposition but a result of the electrode process, for chromium has not been obtained satisfactorily from a bath containing chromous ion only⁷⁾.

The experiments reported here were not concerned with the problems about the anodic process. In the chloride bath, 18-8 Cr-Ni steel is dissolved by an anodic current efficiency over 100%, due to the chemical dissolution. It seems to be advisable for the commercial operation that the cell is e-

quipped with two anodes, one of which is an insoluble anode, separated from the catholyte by a diaphragm, through which desirable current will flow without any change of catholyte composition. Under this scheme, suitable amounts of hydrochloric acid might be supplied to the bath to keep the solution at constant pH.

It will be desirable to minimize the micro cracks occurred in the deposit layers by adding some agents, and this is now under investigation in the authors' laboratory.

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