84

SUR/FIN

American Electroplaters' Society
SUR/FIN '84

71st Annual Technical Conference



July 16-19, 1984
New York Hilton
New York, NY

Session N - Alloy Plating II

AMERICAN ELECTROPLATERS' SOCIETY, INC.

71ST ANNUAL TECHNICAL CONFERENCE - NEW YORK CITY

ALLOY PLATING II

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ELECTRODEPOSITION OF STRESS-FREE Ni-Fe ALLOYS FROM SULFAMATE BATH

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ABSTRACT

Electrodeposition of Ni-Fe alloys containing 10-50% Fe has been carried out from a sulfamate bath. (Ni 81 g/l, Fe 1-7 g/l, citric acid 0.6 g/l, and saccharin 0.5 g/l, pH 3.0, 50°C). Ductility of the Ni-Fe alloy deposits increased with an increase of the thickness of the deposits, however, the Fe content of the alloy deposits does not seem to affect the ductility of the deposits.

The hardness of the Ni-Fe alloy deposits containing 25% Fe was found to be 560 Hv which is higher than that of pure Ni deposit.

The stress-free Ni-Fe alloy deposit was obtained when the Fe content of the alloy is 11.0 wt.%, and these types of the Ni-Fe alloy deposits can be applied for the electroforming.

INTRODUCTION

There has been considerable interest in the electroplating of Ni-Fe alloys as a replacement for bright nickel in the decorative coatings on steel and other substrates[1-9]. These types of the Ni-Fe alloy deposits seemed to have high hardness (Hv 580-680), good ductility, better leveling action and brightness, therefore, there are many practical applications in electroplating industry.

Most of the Ni-Fe alloy plating processes except in permalloy plating, adopted the sulfate-chloride systems as an electroplating bath.

The nickel sulfamate bath has been known as one of the best plating bath to produce the low stress Ni deposits[10], therefore, the sulfamate Ni-Fe alloy plating bath seemed to be suitable for the production of stress-free Ni-Fe alloy deposits.

Even though the anomalous codeposition of Fe with Ni has been discussed in many instances, the mechanism of the codeposition of Ni-Fe has not been fully elucidated[11-12]. It is interesting, therefore, to study the electrodeposition of Ni-Fe alloys in a sulfamate bath from the theoretical point of view, as well as for the practical applications in electroforming.

In the present study, an attempt was made to elucidate the mechanism of the Ni-Fe alloy deposition and to establish the plating variables suitable for the formation of the stress-free Ni-Fe alloy coatings.

EXPERIMENTAL

Electrolyte used in the present study is shown in Table 1. The solution was made up of Ni and Fe sulfamate (Nihon Kagaku Sangyo Co. Ltd.) and conductivity water. The cathode used for the polarization measurement was a copper disc ($1.0 cm^2$) which has been electroplated with Ni-Fe alloys at a current density of 2 A/dm^2 for 5 min.

The Ni-Fe alloy deposits were analyzed by the standard colorimetric techniques after dissolving the alloy deposits in 6N H_2SO_4 + H_2O_2 (30 %).

The cathodic polarization curves in the electrodeposition of Ni-Fe alloys as well as pure nickel were measured by the galvanostatic method at 50 ± 0.5°C.

Ductility of the Ni-Fe alloy and pure nickel deposits was measured by the mechanical bulge type ductility tester[11]. The hardness of the electrodeposited Ni-Fe alloy coatings (60 μm) plated on stainless steel substrate was measured by the microhardness tester (Shimadzu seisakusho Ltd., Type M) with 200 g load for 15 s. The same Ni-Fe alloy films used for the measurement of ductility was subjected to the X-ray diffraction

analysis. The X-ray diffraction measurement was carried out by Fe Kα radiation (λ = 1.936 A) using Mn filter with 30 Kv-7 mA.

A spiral contractometer (Kameras Instruments, U. S. A.) was used for the measurement of the stress of Ni-Fe alloy deposits. The separate anode system consisted of 4 sulfur activated nickel anodes (0.6 dm x 1.0 dm) and 2 iron anodes (0.2 dm x 0.9 dm) was used to keep the constant bath composition during the prolonged electroplating.

Internal stress of the deposits was evaluated from the following expression:

$$S = \frac{2K}{pt} \times \frac{D}{d} \quad (kg/cm^2)$$

where; S: the internal stress (kg/cm^2)
p: spiral pitch (cm)
t: thickness of the base metal (cm)
D: deflection at the centre of the cathode
d: thickness of the deposit (cm)
K: deflection coef. of the spiral

The value of K was estimated to be 3.8×10^{-4} in this experiment, therefore, S was calculated by the following equation.

$$S = 0.127 \times \frac{D}{d} \quad (kg/cm^2)$$

The heat treatment of the electrodeposited Ni-Fe alloys was carried out at 200, 300, 400 and 500 °C in vacuo by using an electric furnace. When the heat treatment was completed, test pieces were cooled in an furnace to room temperature.

RESULTS AND DISCUSSION

(1) Factors affecting the electrodeposition of Ni-Fe alloys.

The Fe content of the alloy deposits increased linearly with an increase of the concentration of Fe^{2+} ion in the plating bath in the current density range of 5-30 A/dm^2 as shown in Fig. 1.

The Fe content of the Ni-Fe alloy deposits obtained from the bath containing various amounts of Fe^{2+}, always in the upper part of the C.R.L.(concentration reference line), and these results imply that the deposition of Fe is preference to the deposition of nickel and these phenomena were much more pronounced in the lower current density region to give the more steep slope of the line.

The effect of the current density on the Fe content of the Ni-Fe alloy deposits is shown in Fig. 2. The Fe content of the Ni-Fe alloy deposits increased with an increase of the current density up to 4 A/dm^2 , however, further increase in the current density resulted in the slight decrease of the Fe content and the Ni-Fe alloy composition is still above the C.R.L., even when the current density is 30 A/dm^2.

The cathodic polarization curves in the electrodeposition of nickel and also of Ni-Fe alloys are given in Fig. 3. The polarization curves for the Ni-Fe alloy deposition were found to shift to the less noble potential and the increased polarization of the alloy deposition was noted with an increase of the concentration of the Fe^{2+}ion in the baths. These results can be explained by the suppresion of nickel discharge by the formation of $Fe(OH)_2$ in the vicinity of the electrode surface[11]. As can be seen in the partial current-potential curves for the electro-deposition of Fe, the limiting current density for the deposition of Fe seemed to become larger in the current density range of 2-4 A/dm^2, and the polarization of the Fe deposition was found to become greater than that of Ni deposition. These results are well accord with the phenomena in which the Fe content of the Ni-Fe alloy deposits gave the maximum value at the current density of 2-4 A/dm^2. Moreover, in the lower current density region such as in 0.2-0.5 A/dm^2, the cathodic current corresponding to the Ni-Fe alloy deposition was found to become larger than that of the pure nickel deposition.

These phenomena can only be observed when the current is exceptionally small, therefore, the current observed in these cases might be due to the reduction of $Fe^{3+}$and/or reduction of H^+

ion in the plating bath.

(2) Properties of the electrodeposited Ni-Fe alloys

As will be seen in Fig. 4, the hardness of the Ni deposits obtained from the sulfamate bath without any addition agents decreased with an increase of the current density and an abrupt decrease in the hardness was observed above the current density of 2 A/dm^2, and then to give a constant value of Hv. 180.

On the other hand, the hardness of the bright nickel deposits obtained from the same type of the plating bath containing citric acid and saccharin increased with an increase of the current density up tp ca. 5 A/dm^2, then to give the almost constant value (Hv 480).

The hardness of the Ni-Fe alloy deposits, however, increased with an increase of a current density up to 5 A/dm^2, then remained a constant value (Hv 550).

In genneral, the Ni-Fe alloy film is harder than that of the nickel deposits, and the hardness of the alloy deposits was hardly influenced by the current densities. The relationship between the hardness and the Fe content of the Ni-Fe alloy deposits obtained from the various Fe^{2+} concentration bath is shown in Fig. 5 as a function of the current density. The Ni-Fe alloy deposits (Fe 5-30 wt%) obtained at a current density of 2.0 A/dm^2 gave rise to rather high hardness (Hv 545), however, the hardness of the alloy deposits seemed to decrease with an increase of the current density.

The internal stress of the electrodeposited films is one of the important mechanical properties for the application of metallic coatings in many industrial fields.

The internal stress of the Ni and Ni-Fe alloy films obtained from the sulfamate baths with or without addition agents is given in Fig. 6 as a function of the film thickness. Pure nickel deposits obtained from a plain sulfamate bath at a current density of 2.0 A/dm^2 was found to be almost stress-free, however, tensile stress of the same deposits increased with an increase of the current density up to ca. 10 A/dm^2. On the other hand, the

internal stress of the Ni-Fe alloy deposits obtained from the same type of sulfamate baths containing citric acid and saccharin was found to be compressive and there seemed no influence of the current density on the internal stress as shown in Fig. 6.

The internal stress of the Ni-Fe alloy films is given in Fig. 7 as a function of the Fe content of the alloy deposits. The Ni-Fe alloy deposits tested in Fig. 7 were prepared from the different alloy plating baths with a different current density to give the definite composition of the Ni-Fe alloys.

The linear relationship between the internal stress and the Fe content of the alloy deposits was observed for the alloy films containing 5-27 wt% Fe, however, no definite relation was observed in the stress and a current density. An extrapolation of the linear part of the curve in Fig. 7 gave the same internal stress observed in the Ni deposit obtained from the Ni plating bath containing citric acid and saccharin.

These results imply that the linear relationship between the internal stress of the Ni-Fe alloy deposits and the Fe content of the alloys is prevailing in the Ni-Fe alloy systems and the Ni-Fe alloy coatings containing ca. 11.0 wt% Fe is always stress-free. An increase in the Fe content of the Ni-Fe alloy deposits resulted in the gradual changes in stress from compressive to tensile, however, there seemed no influence of the current density on the internal stress of the Ni-Fe alloy deposits.

The surface appearance and cross-sectional views of the electrodeposited Ni-Fe alloys containing 11.0% Fe (ca. 400 μm) are shown in Fig. 8. The lamellar microstructure is characteristics of the Ni-Fe alloy deposits obtained from the bath containing citric acid and saccharin[13]. These Ni-Fe alloy deposits have a smooth and bright surface with some granular spot. The banded structure of the Ni-Fe alloys seemed to be attributable to the alternative deposition of each component of the bath, that is nickel and iron. The Ni-Fe alloy coating referred in Fig. 8 was found to be stress-free even in the greater thickness of the deposists.

X-ray diffraction patterns of the Ni-Fe alloy deposits are shown in Figs. 9-11. The Ni-Fe alloy deposits listed in Fig. 9 were prepared from the different baths at a current density of 5 A/dm^2. The X-ray diffraction lines corresponding to Ni(200) and (111) facets seemed to become broad and the diffraction peaks of each plane shifted towards lower angle with an increase of the Fe content of the alloy deposits. These results can be explained by the facts that the crystallite of the alloy deposits is getting small and the stress of the alloy deposits increased due to the formation of the solid solution of Ni-Fe alloys.

The X-ray diffraction patterns of the Ni-Fe alloy deposits containing 11 wt% Fe obtained from the alloy plating baths containing different amounts of Fe^{2+} ion at the various current densities are shown in Fig. 10. Even though the current density for the preparation of Ni-Fe alloy deposits is different, the X-ray diffraction of each alloy deposits seemed to give the same peaks corresponding to the Ni(200) and (111).

The diffraction peaks corresponding to the Ni(200) and (111) facets of the Ni-Fe alloy deposits were found to shift to the lower angle with an increase of the Fe content of the Ni-Fe alloys as shown in Fig. 11.

The orientation of the Ni-Fe alloy deposits was influenced by the current density and the preferred orientatiion of the Ni(111) was observed with increased current density. These results imply that the internal stress of the Ni-Fe alloy deposits does not seem to be influenced by the current density, but the Fe content of the Ni-Fe alloy deposits may be attributable to the internal stress of the deposits.

The effect of heat treatment on the hardness of the Ni-Fe alloy deposits was shown in Fig. 12. Decreease in the hardness of the Ni-Fe alloy deposits was observed in the temperature range of 300-400 °C, however, the hardness of the Ni-Fe alloy deposits obtained from the bath containing citric aid and saccharin decreased sharply upon the heat treatment at about 200-300 °C. Decrease in the hardness of the Ni-Fe alloy deposits in the heat

treatment seemed to be less pronounced in the case of Ni-Fe alloy deposits compared with the bright Ni deposits obtained from the nickel sulfamate bath containing citric acid and saccharin.

The X-ray diffraction patterns of the Ni-Fe alloy deposits (Fe 11%) are given in Fig. 13 as a function of the heat treatment temperature. The intensity of the X-ray diffration peaks for the Ni-Fe deposit (Fe 11%) increased with the heat treatment at 300°C.

These results imply that the heat treatment resulted in the recrystallization of the Ni-Fe alloy deposits depending on the Fe content of the alloy deposits. Decrease in the hardness of the Ni-Fe alloy deposits upon the heat treatment seemed to be attributable to the recrystallization of the alloy deposits.

CONCLUSION

Factors affecting the physical properties of the Ni-Fe alloy deposits obtained from a sulfamate bath have been discussed as a function of the plating variables, and the results are summarized as follows:

1) In the electrodeposition of Ni-Fe alloys, the deposition of nickel seemed to be suppressed by the presence of Fe^{2+} ion and the Fe content of the Ni-Fe alloy deposits always is higher than that of the expected amount based on the composition of the alloy plating baths in the current density range of 1-30 A/dm^2. Anomalous codeposition of Fe seemed to be prevailing in the Ni-Fe alloy plating systems.

2) The composition of the Ni-Fe alloy deposits was influenced by the current density and the Fe content of the Ni-Fe alloy deposits was found to become maximum in the current density of 2-4 A/dm^2.

3) The cathodic polarzation measurements in the Ni-Fe alloy deposition as well as in the pure Ni deposition revealed that the deposition of Ni was suppressed by the presence of Fe^{2+} ion in the vicinity of the cathode. An increase in the current density resulted in the concentration polarization due to the depletion

of Fe ion in the current density range of 2-4 A/dm^2, and the Fe content of the Ni-Fe alloy deposits seemed to decrease with an increase of the current density. In the lower current density region, the cathodic currents corresponding to the reduction of dissolved oxygen and hydrogen ions as well as Fe^{3+} ion have been detected.

4) Smooth and bright Ni-Fe alloy deposits were obtained from the alloy plating bath containing citric acid and saccharin and the hardness of the alloy deposits was found to decrease when the Fe content of the Ni-Fe alloy deposits is more than 30 wt%.

5) The internal stress of the Ni-Fe alloy deposits was hardly affected by the current density, and the linear relationship between the internal stress and the Fe content of the alloy deposits was obtained. Internal stress of the Ni-Fe alloy deposits changed from compressive to tensile with an increase of the Fe content of the alloy deposits, and the stress-free Ni-Fe alloy deposit was obtained when the Fe content of the alloy is 11.0 wt%.

6) The orientation of the Ni-Fe alloy deposits was influenced by the current density and the preferred orientation of the Ni(111) was observed with an increase of the current density.

7) An X-ray diffraction analysis of the Ni-Fe alloy deposits revealed that the shift in the diffraction lines could hardly be influenced by the current density. The diffraction peaks corresponding to Ni(200) and (111) were found to shift towards the lower angle with an increase of the Fe content of the Ni-Fe alloy deposits. These phenomena seemed to be well accord with the fact that the linear relationship was observed between the Fe content and the stress of the alloy deposits.

8) The hardness of the Ni-Fe alloy deposits decreased when the alloy deposits were received heat treatment, however, the influence of the heat treatment on the hardness of the alloy deposits seemed to be less pronouced compared with the bright nickel deposits obtained from the same type of the bath with the addition agents. Decrease in the hardness of the alloy deposits

seemed to be due to the recrystallization of the Ni-Fe alloys.

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Table. 1 Bath composition

$Ni(NH_2SO_3)_2 \cdot 4H_2O$*	450 g/l
Fe(as Ferrous sulfamate)*	0-7 g/l
H_3BO_3**	45 g/l
Citric acid**	0.6 g/l
Saccharin	0.5 g/l

* Products of Nihon Kagaku Sangyo,Co.,Ltd.

** Products of WAKO PURE CHEMICAL INDUSTRIES,Ltd.

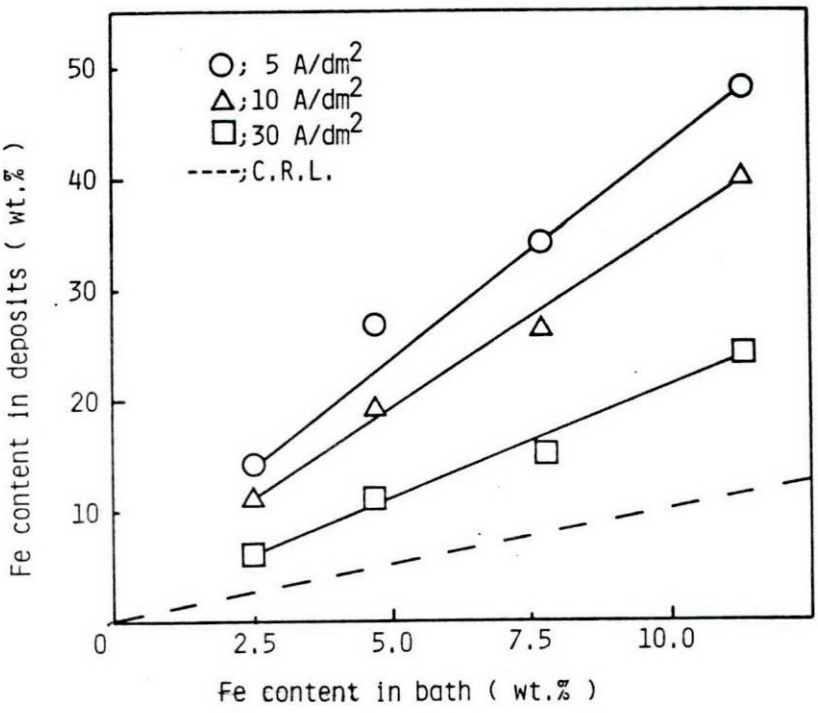

Fig.1 Effect of Fe^{2+} concentration in the bath on the Fe content of the Ni-Fe electrodeposits

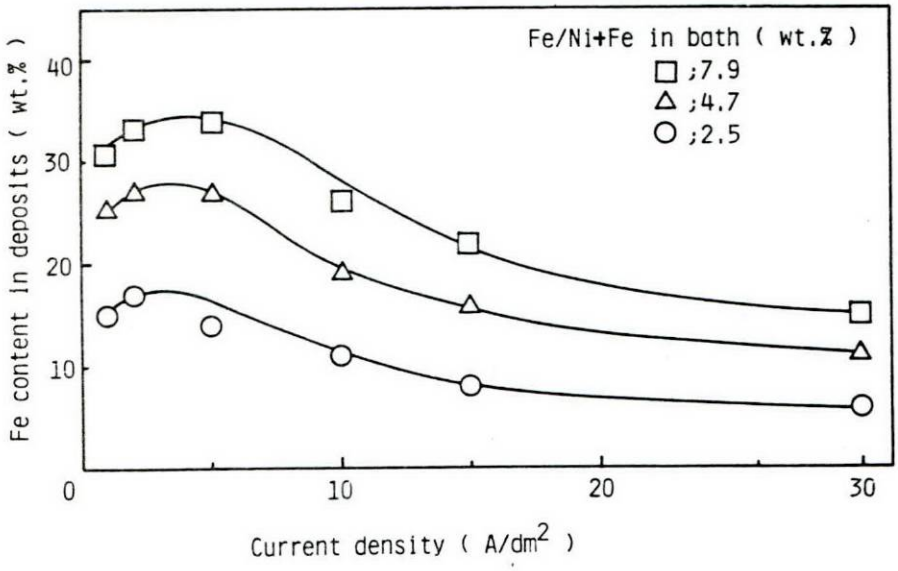

Fig.2 Effect of current density on the Fe content of Ni-Fe alloy deposits

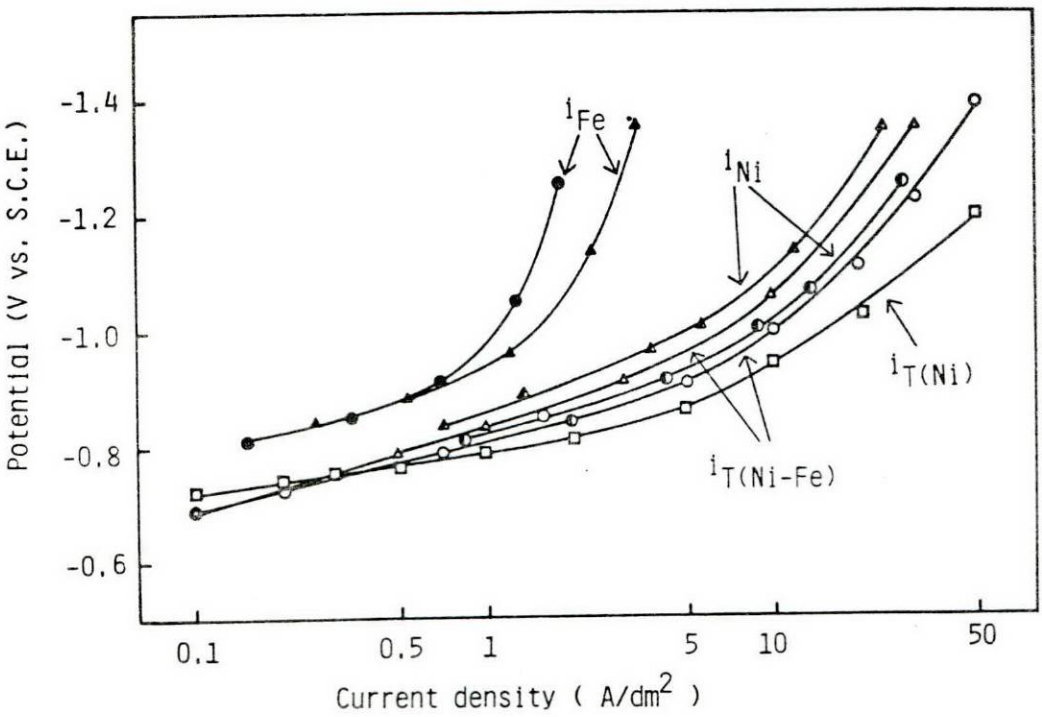

Fig.3 Cathodic polarization curves in the electrodeposition of Ni and Ni-Fe alloys

Total current , iT
□ ; Ni bath(Ni, 82.0 g/l), ○ ; Ni-Fe bath(Fe, 2.1 g/l), △ ; Ni-Fe bath(Fe, 4.3 g/l)
Partial current in Ni-Fe bath
◐ ; iNi(Fe, 2.1 g/l), ◭ ; iNi(Fe, 4.3 g/l)
● ; iFe(Fe, 2.1 g/l), ▲ ; iFe(Fe, 4.3 g/l)

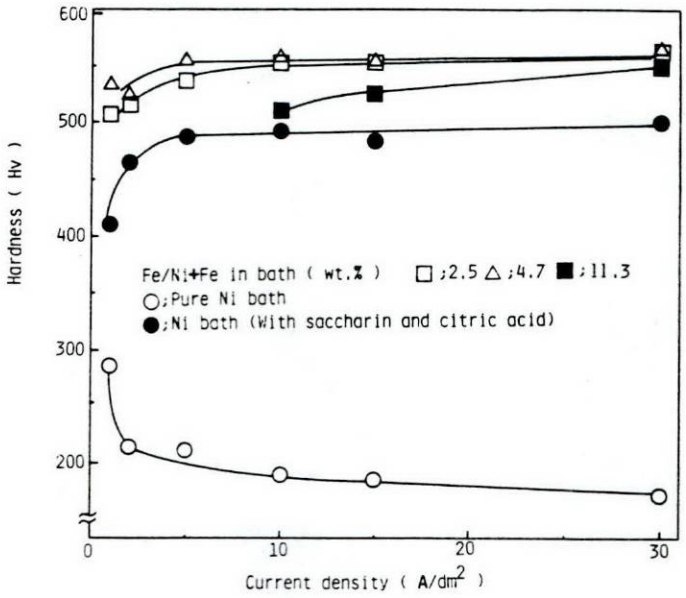

Fig.4 Effect of current density on the hardness of Ni and Ni-Fe alloy deposits

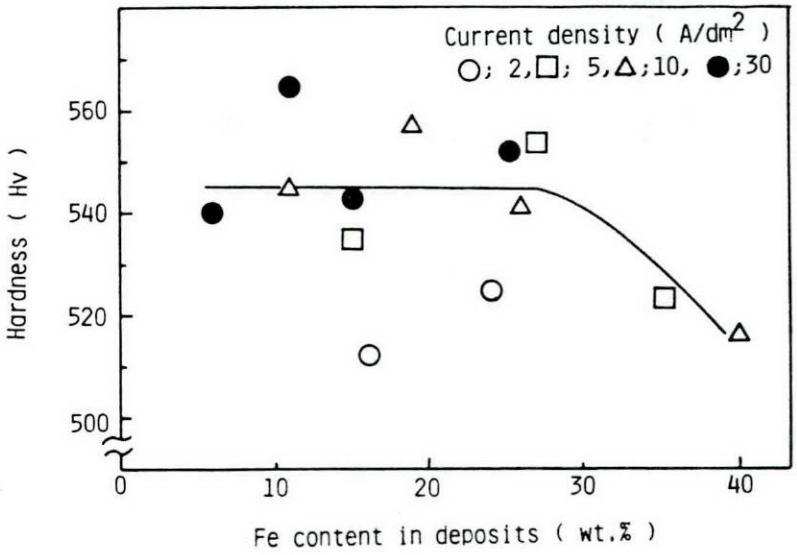

Fig.5 Effect of the Fe content on the hardness of Ni-Fe alloy deposits

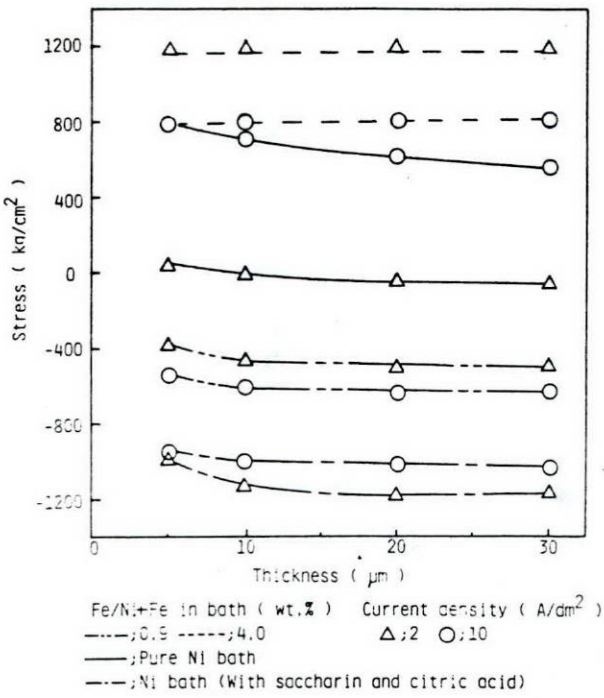

Fig.6 Effect of film thickness on the internal stress of Ni and Ni-Fe alloy deposits

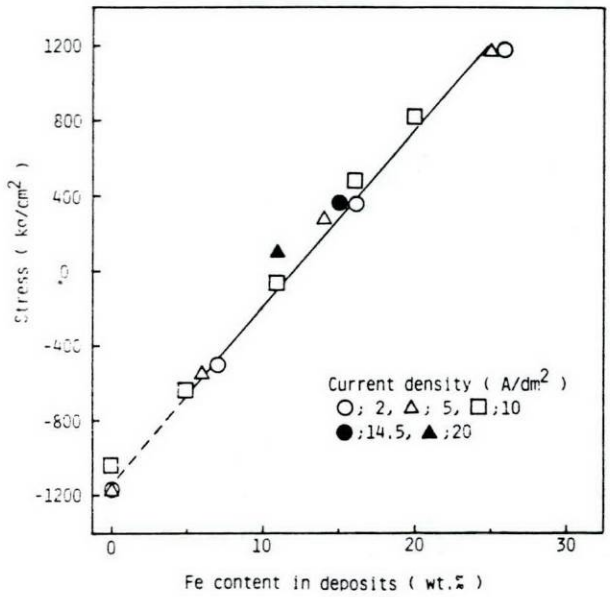

Fig.7 Effect of the Fe content on the internal stress of the Ni-Fe alloy deposits

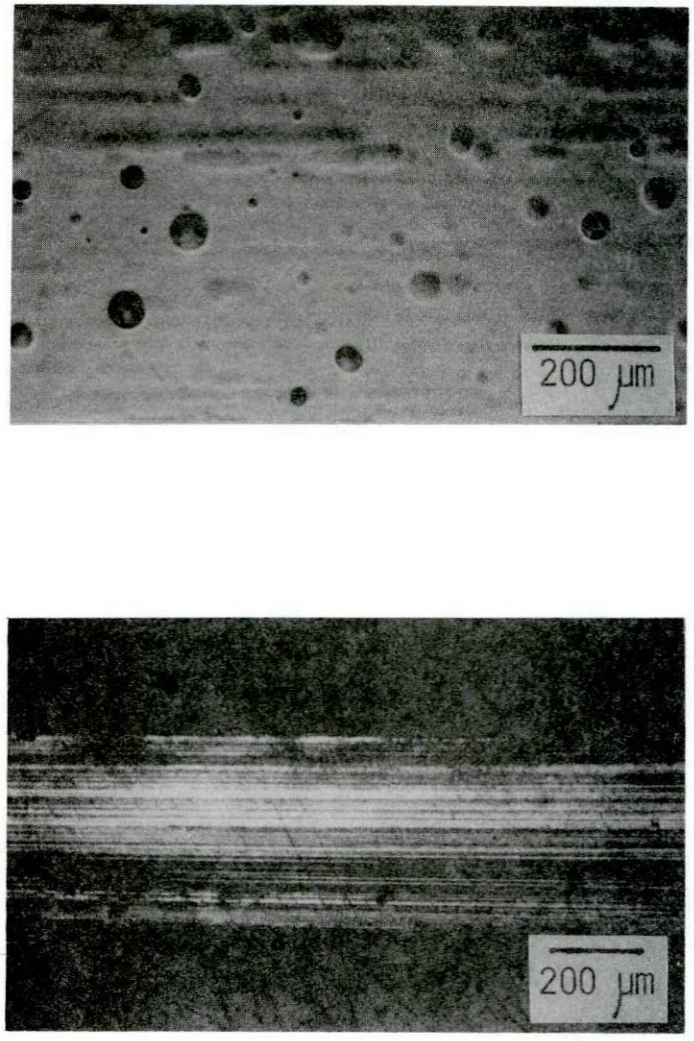

Fig. 8 Surface appearance and cross-sectional views of the electrodeposited Ni-Fe alloy

Plating bath

Ni sulfamate	450 g/l	(Ni, 81.3 g/l)
Fe sulfamate	11.5 g/l	(Fe, 2 g/l)
Boric acid	45 g/l	
Citric acid	0.5 g/l	
Saccharin	0.5 g/l	

pH 3.0, 50°C, 10 A/dm², 6h
Fe content of Ni-Fe alloy, 11.0%

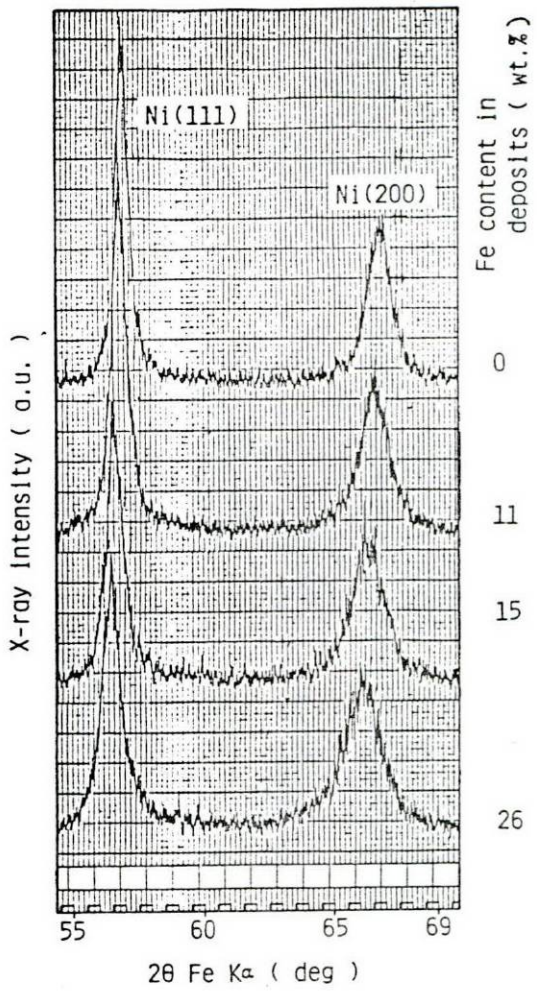

Fig.9 X-ray diffraction patterns of Ni-Fe alloy deposits (5 A/dm^2)

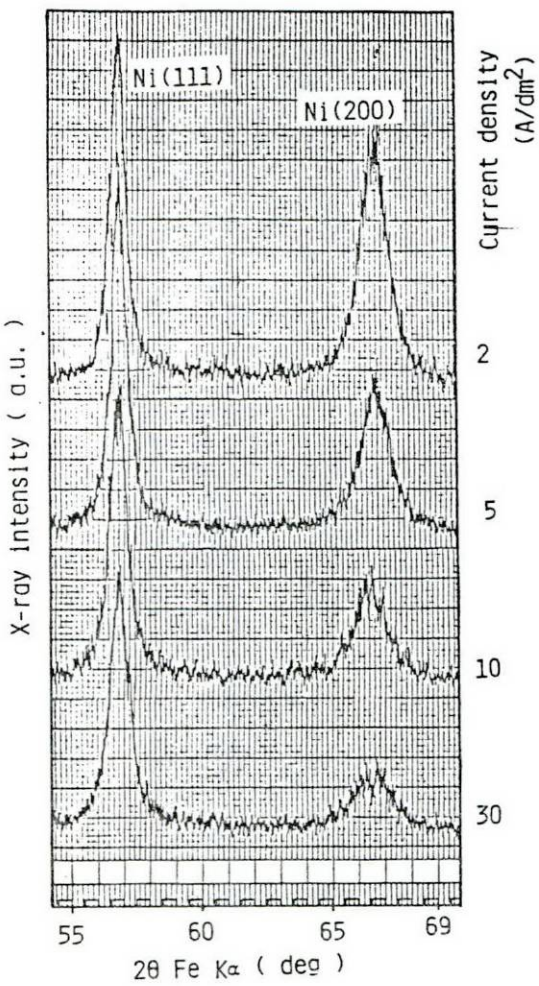

Fig.10 X-ray diffraction of the Ni-Fe alloy deposits (Fe, 11 wt.%)

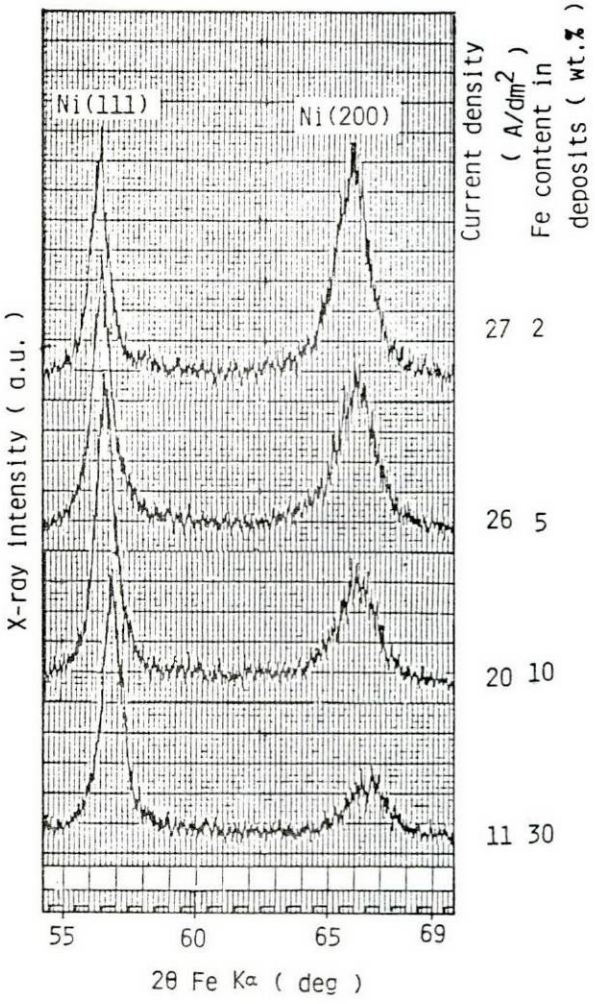

Fig.11 Effect of current density on the X-ray diffraction of the Ni-Fe deposits (Fe content in bath, 2.3 %)

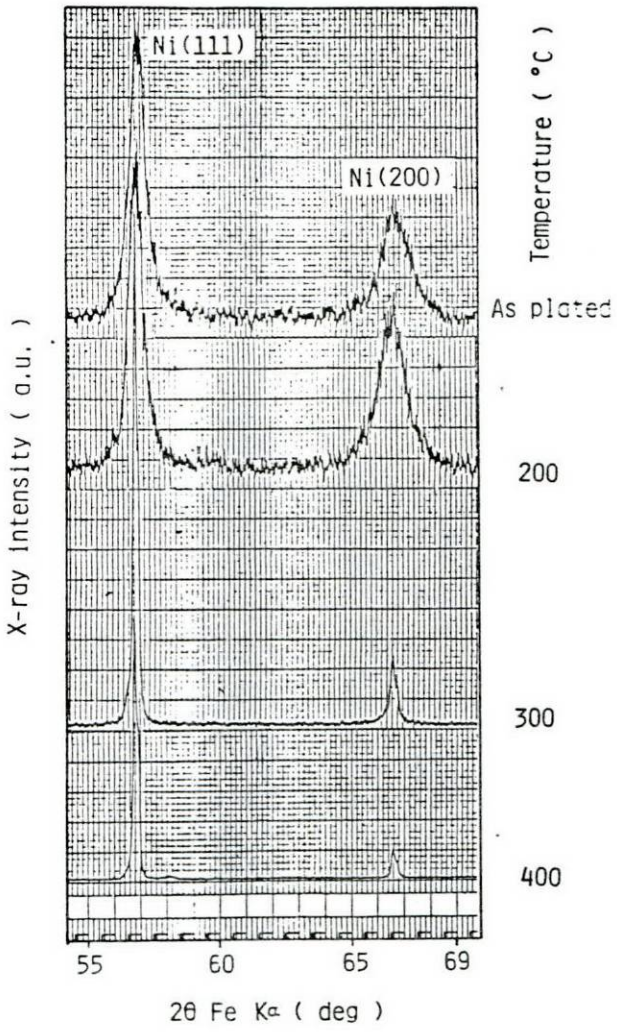

Fig.13 Effect of heat treatment on the X-ray diffraction of the Ni-Fe deposits (5 A/dm², Fe content, 11 wt.%, heat treatment, 2h, in vacuo)

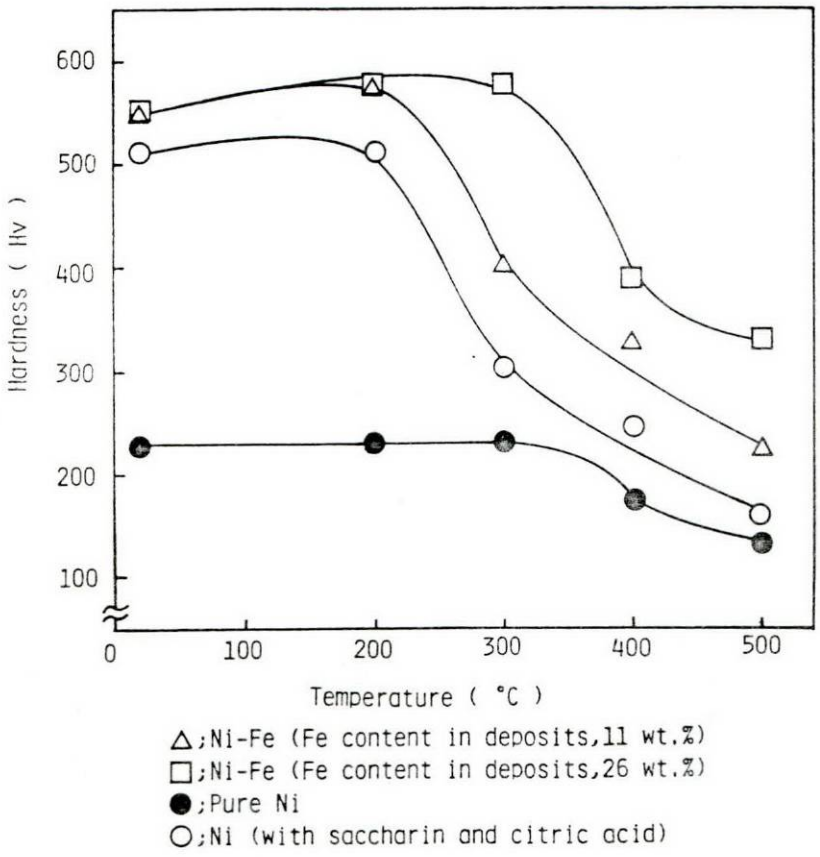

Fig.12 Effect of annealing temperature on the hardness of Ni and Ni-Fe electrodeposits (5 A/dm^2)

N-2

Alloy Plating II
Session N

Investigation of Zinc-Nickel Alloy Electrodeposits - Part 1. Rack Plating

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Investigation of Zinc-Nickel Alloy Electrodeposits — Part 1. Rack Plating

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INTRODUCTION

Traditionally, zinc has been the most widely used electrodeposit for protecting steel from the ravages of corrosion. In a corrosive environment, this inexpensive sacrificial metal corrodes preferentially and protects the underlying steel. To enhance its protective ability, the zinc electrodeposit is usually given a post-plating chromate conversion coating.

This iridescent chromated zinc (289 Finish) has been successfully used in a wide variety of Bell System applications for many years. However, in certain applications, particularly those where close metal-to-metal spacings that must remain electrically isolated occur, the use of a zinc electrodeposit, whether chromated or not, may lead to a problem not related to corrosion.

For example, the Remreed shunt plates, Ferrod sensor covers, and 80C apparatus mounting hardware used in 1A technology were all originally protected against corrosion using the 289 iridescent chromated zinc finish. Unfortunately, zinc, like cadmium and tin, has a tendency to spontaneously grow filamentary "metallic whiskers." These whiskers, bridging between closely spaced metal conductors, can carry currents up to 25mA and cause either momentary or permanent electrical shorts. Because of the problems whiskers might cause if used on the shunt plates, covers, and apparatus mounting hardware, zinc was replaced by nickel, a significantly (about ten times) more expensive but whisker immune electrodeposit. While eliminating the whisker growth problem, the use of the nickel electrodeposit resulted in increased part costs with no corresponding increase in corrosion protection over that afforded by the previously used zinc deposit.

In the case of tin and its alloys, a long term (20 year) investigation (1) has shown that electrodeposited tin alloys such as tin-lead and tin-nickel have little or no tendency to grow spontaneous whiskers, even though unalloyed electrodeposited tin represents such a high whisker growth risk that its use in Bell System applications has, for many years, been restricted, requiring written permission of appropriate consultants before it can be specified. This significantly reduced tendency of tin alloys to grow whiskers, has been confirmed in at least one other investigation of tin-lead alloys (2). If a similar tendency were found for electrodeposited alloys of zinc, it would permit the use of a less expensive deposit than nickel in applications where whisker growth has prevented the use of unalloyed zinc electrodeposits.

Early work relative to the protection of steel using a combination of zinc and nickel involved the electrodeposition of separate zinc and nickel layers that were subsequently thermally diffused to form an alloy. This process is known by the trade name Corronizing.® (3)

Over 75 years ago, zinc containing up to about 30 weight percent nickel was successfully deposited from a sulfate based plating solution (4). Additional plating solutions that have been used include chloride (5), sulfamate (6), pyrophosphate (7), and cyanide (8) based systems. Usually zinc-nickels deposited from cyanide based solutions have a lower nickel content (~0.5 to 2w/o) than those deposited from systems without cyanide (~5 to more than 40 w/o) (8). Over the years, a number of patents (5, 8-12) have been issued for zinc-nickel alloys deposited from various plating solutions.

Zinc-coated steel sheet has been widely used for enhancing the corrosion resistance of automobile bodies. Although the application of increased zinc thicknesses could offer the additional corrosion protection required for increased warranty periods, such thickness increases not only increase the weight of the car, thus reducing gas mileage, but also introduce forming and welding difficulties (13).

For equivalent thicknesses, the corrosion protection of electrodeposited zinc-nickel alloys when subjected to a salt spray (fog) test similar to ASTM B 117, has been reported to be up to seven

times greater than that of unalloyed zinc deposits (8,13,14,15). As shown in Figure 1 (14), although the corrosion resistance of zinc-nickel is better than zinc for a wide range of nickel content, it appears to reach a maximum at about 14 w/o nickel (8,13,14,15). Alloys containing more than about 20 w/o nickel tend to have high tensile stresses, are brittle (5), and have galvanic potentials more noble than those of iron and steel, all undesirable characteristics. From about 5 to 15 w/o nickel, the deposits are reasonably ductile, are slightly stressed in compression, have potentials that are anodic to those of iron and steel, and appear to protect the underlying iron or steel better than an equivalent thickness of unalloyed zinc, all desirable characteristics.

The enhanced corrosion resistance of the zinc-nickel alloys compared to unalloyed zinc electrodeposits has led to the increasing use of zinc-nickel electrodeposits in both appliance and automotive applications (13, 14, 15).

Electrodeposits of a zinc-nickel alloy containing about 15w/o nickel from an ammoniacal plating solution were previously evaluated for potential use in the Bell System (16). The results showed that such an alloy was anodic to steel, had a corrosion resistance at least equal to unalloyed zinc, and had no tendency to grow spontaneous whiskers six months after being plated. In this earlier investigation, the cathode current efficiency of the zinc oxide-nickel chloride plating solution, originally studied by S. Ia. Popov (18), was also evaluated, as were the effect of various brighteners, the effect of current density on nickel content of the alloy, and the best method for developing a post-plating passivating chromate treatment.

Recent examination of the whisker study samples from this earlier study has shown that there is still no evidence of spontaneous whisker growth five and one half years after being plated (17). As a consequence, zinc-nickel electrodeposits, like their tin-nickel and tin-lead counterparts, appear to be immune to the spontaneous growth of metallic whiskers.

Renewed interest in the use of a whisker immune electrodeposit that is both anodic to steel and less costly than the pure nickel deposits currently in use led us to undertake an evaluation of rack-plated zinc-nickel deposits from a proprietary solution and rack-plated deposits from a modification of the ammoniacal solution already investigated by Popov (18) and Williams (16). The original solution composition and the plating parameters used by Popov and Williams are shown in Tables I and II. The work reported here covers the rack plating of samples from the modified solution.

EXPERIMENTAL RESULTS

EVALUATION OF MODIFIED AMMONIACAL PLATING SOLUTION

Originally, the authors intended to use the solution described in Table I. However, in numerous attempts, great difficulty was experienced in dissolving the chemicals used to make up the solution. Because of this, it was felt that this solution would add unnecessary problems in production. Therefore, the modified sulfate solution described in Tables III and IV, in which all the chemicals easily dissolved, was used throughout this investigation. This substitution of zinc and nickel sulfates for zinc oxide and nickel chloride was first proposed by Domnikov in 1963 (19).

PLATING OF COPPER PANELS

The first plating experiments were run on copper panels with a nickel sulfate concentration of 22g/L, a pH of 6.8, and various cathode current densities and solution temperatures.

Prior to plating, the copper panels were chemically polished using a bright dip solution (20) containing a mixture of sulfuric, nitric, and hydrochloric acids and water.

ANALYSIS OF ZINC-NICKEL DEPOSIT

Copper panels (1/2"x5/8"x1/32") were weighed after being plated with the zinc-nickel alloy. The deposit was stripped in 30mL of warm 1:1 HCl and the panels reweighed to obtain the weight of zinc-nickel deposited. The 30mL of solution containing the dissolved alloy were diluted with DI water to 50mL. Depending on the weight of the deposits dissolved in the solutions, they were diluted further to bring the amount of metal in the solution within the appropriate range for analysis by

atomic absorption spectrometry. For the purposes of this final dilution, it was assumed that all deposits contained about 20 weight percent nickel.

RESULTS

Table V shows the results of this first plating experiment. As can be seen from the table, in general, as Williams (16) found with the zinc oxide-nickel chloride solution, the nickel content of the deposit plated out of the sulfate solution (Table III) increases with increasing temperature and decreases with increasing current density.

The results of additional plating experiments in which the concentration of nickel sulfate in the solution was varied are shown in Tables VI and VII. The effect of the addition of 2g/L of an organic brightener (glycogen) is also included.

While a few anomalies are present in the data in Tables VI and VII, the results essentially show that at both 30°C and 50°C, whatever the nickel sulfate concentration, the weight percent of nickel in the deposit decreases with increasing cathode current density up to about 75 ASF. Cathode current densities above this value appear to result in an increase in the nickel content of the deposit.

With regard to the effect of the concentration of nickel sulfate in the solution on the nickel content of the deposit, it appears that at 30°C for a given cathode current density, 14g/L and 18g/L give about the same amount of nickel. On the other hand, when the nickel sulfate is increased to 22g/L, the nickel content generally tends to be somewhat higher, again up to a cathode current density of 75 ASF.

With the obvious exception of the spurious result for 10ASF at 14g/L, at a temperature of 50°C and a given cathode current density, increasing the nickel sulfate content generally results in an increase in nickel content. Here also, up to about 75ASF and whatever the nickel sulfate concentration, increasing the current density results in decreasing the nickel content of the deposit.

At 30°C, the addition of the brightener glycogen appears to suppress the nickel content in the deposit, at least up to 100ASF. At 50°C, the results are somewhat mixed. However, at both temperatures the glycogen addition does not appear to change the effect of increasing current density on the nickel content of the deposit (i.e., increasing current density gives decreasing nickel content, except at the higher current densities). The glycogen does not appreciably improve deposit appearance at either temperature.

Finally, it may be noted that the current efficiency was found to be relatively constant between 20 and 75ASF, independent of solution temperature, nickel sulfate content, and cathode current density. The time to deposit approximately 0.0015 inch was 10 minutes at 20ASF and 2 minutes and 40 seconds at 75 ASF.

CONCLUSIONS

At 30°C, zinc-nickel deposits with less than 15 weight percent nickel can be produced from solutions with nickel sulfate contents ranging betweent 14 and 22g/L at cathode current densities between 10 and 75 ASF. This should insure a reasonably ductile deposit that is anodic to steel and of sufficiently low stress to permit its use in applications where the use of zinc, due to its potential for spontaneous whisker growth, could be detrimental. At 50°C, the nickel sulfate content should be limited to 14 to 18g/L, while the current density can range between 10 and 100ASF in achieving the same desirable deposit characteristics.

FUTURE INVESTIGATIONS

This part of the investigation has dealt with the effect of varying the plating solution parameters on the nickel content of rack plated deposits. Future investigations are planned to study similar effects with barrel plated specimens. In addition, the corrosion of steel panels plated with the zinc-nickel alloy as well as the best procedures for chromating the deposited alloy will be studied, and other brightener systems will be evaluated.

Table I

Solution Make Up

Chemical	Concentration (g/L)
ZnO	12 — 15
$NiCl_2 \cdot 6H_2O$	12 — 36
NH_4Cl	200 — 300
Boric Acid	15 — 25

Table II

Plating Parameters

Parameter	Range
Temperature	23 — 50° C
pH	6.5 — 6.8
Anodes	Nickel

Table III

Modified Ammoniacal Solution Make Up

Chemicals	Concentration (g/L)
$ZnSO_4 7H_2O$	52 — 55
$NiSO_4 6H_2O$	14 — 22
NH_4Cl	250
Boric Acid	20

Table IV

Plating Parameters

Parameter	Range
Temperature	30 — 50° C
pH	6.5 — 6.8
Anodes	Nickel

Table V

WEIGHT PERCENT NICKEL IN DEPOSIT
(22g/L of Nickel Sulfate)

Current Density	Temperature - °C		
ASF*	30	40	50
5	21.9	29.0	38.7
10	17.1	22.9	25.4
20	17.8	19.4	22.2
30	15.9	20.3	19.9
40	13.0	18.1	20.0
50	11.9	16.3	19.1
75	11.5	13.6	16.4
100	11.1	13.7	15.2

* Amperes per Square Foot

Table VI

WEIGHT PERCENT NICKEL IN DEPOSIT - 30° C

Current Density	Nickel Sulfate (g/L)			
ASF*	14	18	22	22**
5	12.5	12.3	21.9	13.0
10	12.7	10.7	17.1	14.1
20	10.7	10.9	17.8	12.5
30	10.0	10.4	15.9	10.7
40	10.6	11.9	13.0	10.1
50	10.1	10.5	11.9	10.9
75	10.4	15.5	11.5	11.1
100	16.8	13.1	11.1	11.7
200	17.6	X	X	15.7

* Amperes per Square Foot

** +2g/L Glycogen Organic Brightener

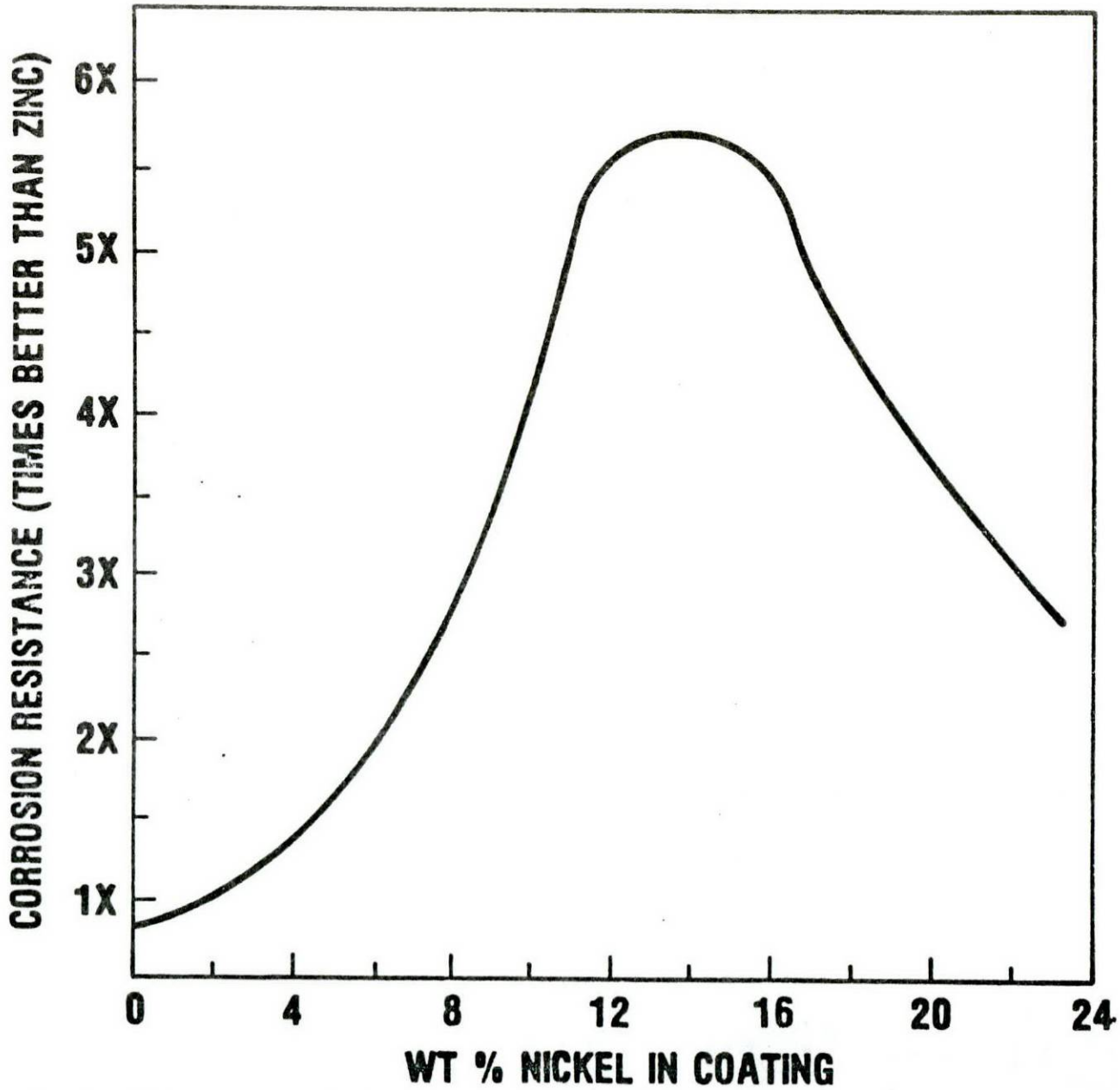
Table VII

WEIGHT PERCENT NICKEL IN DEPOSIT (50° C)

Current Density	Nickel Sulfate (g/L)			
ASF*	14	18	22	22**
5	17.1	16.0	38.7	19.0
10	27.1	14.3	25.4	20.3
20	12.6	13.4	22.2	17.4
30	12.8	13.0	19.9	15.9
40	12.0	13.7	20.0	14.9
50	11.6	13.7	19.1	14.3
75	11.8	13.2	16.4	12.9
100	13.5	13.8	15.2	13.1
200	17.5	18.6	X	18.9

* Amperes per Square Foot

** +2g/L Glycogen Organic Brightener



T. A. HIRT, PROC. 3rd AES CONTINUOUS STRIP PLATING SYMPOSIUM, ANNAPOLIS, MD 1980

Figure 1

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N-3

Alloy Plating II
Session N

Non-Cyanide Brass Plating

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NON-CYANIDE BRASS PLATING

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Since the development of brass plating in the early 1840's there has been a desire to develop a non-cyanide brass plating bath. The need was initially started in recent years to eliminate cyanide from the work place. Only 0.75gm. of Sodium Cyanide can be fatal (1) to an average size person, which is equivalent to 15 milliliters of a basic brass plating solution. History of the industry, however, shows us that the casualty rate from the operation of the cyanide plating bath is very low, in fact, rare. This in itself, is a tribute to our industry. The real concern arises from the disposal of cyanide wastes generated from these baths, a concern that is costing the industry millions of dollars in pollution control equipment and operating costs.

An extensive literature survey on non-cyanide plating systems was done by S.S. Brenner (2). One of the problems he found in codepositing the metals was in finding compounds that formed copper and/or zinc complexes that brought the static potentials close enough together to allow codeposition of the alloying metals. Attempts had been made to produce commercially acceptable electrodeposits through the use of some exotic formulations. For example, other investigators have found copper and zinc alloys can be electrodeposited from baths containing thiosulfates (3), glycerol (4), sulfates (5) thiocyanates (6), oxalates (7), tartrates (8), carbonates (9), pyrophosphates (10), and triethanolamine (11), just to name a few. He found those baths where the deposition potentials of copper and zinc were almost as close together as in the cyanide bath, the properties of the deposits were not satisfactory. In some cases, a preliminary cyanide copper or nickel strike was needed to insure adhesion. In others, the cost of formulations were prohibitive or the deposition range was narrow.

In the development of this process several objectives had to be met before the present invention could prove to be commercially acceptable. First and most important, this bath had to be totally cyanide free. It had to deposit copper and zinc alloys in all proportions. It also had to permit the alloy to be deposited directly on the copper, iron, steel, and zinc alloys customarily used in the industry without requiring a preliminary cyanide copper or nickel strike to insure adhesion. Further, this bath had to deposit the alloy without the spotting of porous areas which can occur when a cyanide bath is employed. Another objective was to make easy the removal of metal ions from the spent solution and make unnecessary the costly cyanide destruction procedure which is required with conventional alkaline cyanide plating baths and their rinses to meet pollution discharge requirements.

The copper and zinc ions supplying the cyanide-free plating bath of interest may come from any water soluable salt such as sulfate, chloride, fluoroborate, fluoride, or fluorosilicate. Other zinc and copper compounds used include carbonates, phosphates, pyrophosphates, hydroxides, and zinc oxide. Especially preferred for use are the mono and polyhydroxy and mono and polycarboxy

aliphatic acid salts of the metals. These salts are not commercially available in large enough quanities to allow there commercial use, however, the salts can be made in situ . It is generally known that as long as metal ions are present, i.e., copper and hydroxide for example, and a carboxylic acid, such as acetic is introduced, the resultant reaction produces the carboxylic aliphatic acid salts of copper and water. Likewise, a mix of zinc oxide and propanoic acid reacts to form zinc propanoate in solution. Therefore, rather than purchasing the metal salts as mono or polyhydroxy mono or polycarboxy aliphatic acid salts, it is preferred to combine the metal salts with the proper amounts of either type of organic acid to form the desired metal complex.

It has been demonstrated in the laboratory that any salt can be used to supply the metal ion, providing the anion does not interfer in the electroplating process. For example, copper and zinc chromates and cyanides would not be suitable as a source of metal ions because the chromate would inhibit the metal deposition and the cyanide would defeat the purpose of the plating bath.

The ratio of copper to zinc ions in the solution can range from 99:1 to 1:99, depending on the nature and properties of the alloy desired. There appears to be no limitations on the ratios of the metals in the mixture than can be deposited.

The chelating agents preferably used in the cyanide-free brass bath are glucoheptonic acid and its alkali metal salts. The chelating or sequestering abilities of the glucoheptonic acid and its salts have been known for some time, but their use was limited in past plating baths to relatively small quanities to chelate small amounts of desirable metals used as grain refiners and brightners or as a means of chelating undesirable metal ions introduced as impurities. In this present bath, the chelating agents are used in much higher quanities which help maintain a reservoir of metal ions of sufficient quanity as to permit the codeposition of the desired alloy over a wide range of operating conditions. It is necessary that this solution contains an amount of chelating agent which is in excess of the stoichiometric equivalent of at least one of the metals, preferably the copper. The chelating agent that is most preferred is the sodium salt of glucoheptonic acid (Sodium 1,2, 3,4,5,6 hexahydroxy hexane -1- carboxylate. If desired, other chelating agents may be added to the bath.

Some examples of these plating baths are as follows: (12)

Copper/Zinc Electrolyte Ratio 90:10

$CuCO_4$	10 gm/l
$ZnSO_4$	1 gm/l
$CH_2OH(CHOH)_5COONa$	20 gm/l
NaOH	40 gm/l

Copper/Zinc Electrolyte Ratio 70:30

$CuCO_3 \cdot Cu(OH)_2$	15 gm/l
$ZnCO_3$	5 gm/l
$CH_2OH(CHOH)_5COONa$	50 gm/l
KOH	35 gm/l

Copper/Zinc Electrolyte Ratio 50:50

$Cu(CH_3COO)_2$	20 gm/l
ZnC_2O_4	16 gm/l
$CH_2OH(CHOH)_5COONa$	30 gm/l
LiOH	45 gm/l

A wide range of temperatures used in the deposition of the copper and zinc alloy were evaluated using the above formulations. Temperatures ranging from approximately 20°C - 65°C are satisfactory.

The preferred make up used in the deposition of 70:30 brass comes from a concentrate having a pH of about 13.0 to 13.5 and containing in each liter about 15 to 60 grams of copper, five (5) to 25 grams of zinc, 80 to 200 grams of potassium hydroxide, and 40 to 300 grams of the sodium salt of glucoheptonic acid as the chelating agent. This mixture is preferably supplied as a concentrate which is diluted with four (4) parts of water to make the plating bath.

The plating bath after dilution has a pH range of 13.0 to 13.5 and may have the following composition:

	Optimum	Range
Cu	6.75 gm/l	3.75 - 15.0 gm/l
Zn	2.25 gm/l	1.25 - 6.0 gm/l
OH	30.0 gm/l	20 - 37.5 gm/l
Chelate	50.0 gm/l	10 - 75 gm/l

The plating solution is made up as follows:

The tank size is calculated (allowing for filter and related heating equipment), and that quanity is divided by five (5). This figure is the amount of concentrate required to make up the bath. The material is added to the tank and water is added to near the final volume. One percent (1%) of a brightner agent is then added (1 gallon per 100 gallons) to the solution. The bath is

ready for operation after a temperature check and a short electrolysis of 10 amps per square foot.

Anodes used in this bath are either 70:30 bar anodes or 70:30 ball anodes in titanium baskets. Steel should not come in contact with the plating solution for it will slowly dissolve under reverse current conditions.

Plating with the cyanide-free brass bath requires all plating tanks and equipment to be totally free of cyanide. Rubber, koroseal, or other plastic tanks are suitable. After removing the old cyanide bath, the equipment should be washed with hypochlorite solution and the tank soaked for 24 hours in two percent (2%) sodium hypochlorite to destroy all remaining cyanide. Hoods, barrels, and filtering equipment must also be free of cyanide. After removal of the hypochlorite solution and rinsing, a dilute sulphuric acid rinse of one or two percent (1-2%) should follow, after which a five percent (5%) caustic rinse is used to neutralize the remaining acid. The caustic is removed and the concentrate is added and diluted for use.

Control of the caustic level is the most important and frequent adjustment required. The caustic should be checked daily (this replaces the cyanide check in a conventional brass tank). The check only takes a few minutes and should not be ignored. Control of the caustic is very important for proper anode corrosion. Liquid potassium hydroxide is used for correcting the caustic in the bath and is preferred for its ease of addition.

The metal content of the bath is simply replenished by adding the bath concentrate whenever the copper metal content decreases below its optimum range. Adding the bath concentrate also adds caustic, therefore caustic adjustments should be made after the metal additions, if required. Adding the concentrate will automatically adjust the other chemical components.

The brightner additions are determined by ampere hours plating. One gallon of brightner solution is added for every 12-15,000 ampere hours. For best and most economical results, an automatic brightner feed or additions every four hours is advisable. A dark smutty deposit could indicate a high brightner content (assuming correct bath composition) and a low content results in loss of proper yellow-green color.

The determination of the three main components, the copper, zinc, and caustic are done simply by wet chemical analysis. Although the basic principles of this analysis have been known for some time, the procedures have been modified by our labs especially for this process and can be completed in about 20 minutes.

The analytical procedure employed are as follows:

1. Zinc Metal

   a) Place 10 ml. sample in 250 ml. flask.

   b) Add 50 ml. deionized water.

c) Add 0.5 grams of Sodium Cyanide (NaCN) and swirl until completely dissolved. Let stand for 10 minutes. (At this point solution will be clear).

d) Add a small amount of Eriochrome Black T Indicator (solution should now be a bright pink color).

e) Add 5 grams of Chloral Hydrate and swirl vigorously for at least 30 seconds. While swirling, the solution will turn from a clear pink to a cloudy blue violet to a clear red violet color. Titrate immediately with 0.1M E.D.T.A.

f) Titrate to a blue color change. Reading should be taken quickly as the end point is fugitive.

Calculations: (mls. of 0.1M E.D.T.A.) X 0.087 = oz/gal Zn Metal

2. Copper Metal

a) Place 5 ml. sample in a 250 ml. flask.

b) Add 50 ml. of deionized water.

c) Add 2 or 3 grams of ammonium persulphate.

d) Add 5 ml. of ammonium hydroxide and allow to stand for 10 minutes.

e) Add 10 drops of pan indicator (don't add an excess of 10 drops for the end point is affected).

f) Before titrating, add 5 grams of chloral hydrate, swirl to dissolve crystals.

g) Titrate immediately with 0.1M E.D.T.A. solution to an apple green end point.

Calculations: (1.74 X (mls. of o.1M E.D.T.A.) divided by 5,

minus (2 X (the zinc metal in 1) X 0.488 =

oz/gal. Cu Metal

3. Potassium Hydroxide

a) Place 5 ml. sample in 250 ml. flask.

b) Add 10 ml. of deionized water.

c) Add three to five (3 to 5) grams of sodium cyanide (NaCN) and swirl. Solution should now be clear to pale green.

d) Add 8 to 10 drops of LaMotte Sulfo Orange indicator and 1 or 2 drops of Alkali Blue indicator.

e) Titrate with 1.0N HCl to a green end point.

Calculations: (mls. of 1.0N Hcl) X 1.5 = oz/gal. KOH.

A convenient process for removing metal ions from a spent bath or rinse tank of the non-cyanide bath involves introducing carbonate ions into the spend bath. The pH of the solution is lowered to about 8.5 and a reduction of chelating power causes the metals to precipitate as metal carbonates allowing for easy removal as sludge. The remaining organic ions are carboxylic aliphatic acid salts which are relatively non-toxic. Many of these salts are used in food preservatives or are contained in large quantities in natural foods.

In the process of plating objects, the tank voltages and amperages used are similar to those used on cyanide processes: 2-6 volts on tank or rack operations and 9-12 volts on barrel operations. The plating temperature of the non-cyanide bath is preferably 100°F. Either mild air or cathode rod agitation is used in rack plating. Barrel plating is done at 2-4 RPM's. For best results continuous filtration is needed for smooth plating and the filter should be lined or of non-metallic construction. Ventilation is required because of the caustic nature of the bath.

Although cyanide-free brass bath may be used for barrel plating, or with air or cathode rod agitation for rack plating heavy brass. Ball burnishing is required for a bright finish. It may be oxidized and relieved for antiqued finishes. At present it is not suitable for flashing over nickel. Cyanide-free brass may be plated directly on steel or zinc based die castings, without a preliminary strike in barrel or rack operations. It has also been demonstrated that this bath can be used as a strike before non-cyanide alkaline copper plating to insure proper adhesion of the copper. Laboratory experiments have also indicated the possibility that non-cyanide brass could eliminate the need for the cyanide copper strike before acid copper plating, thus eliminating cyanide completely from the work place.

The plate of the alloy obtained through this bath is uniform and acceptable for many purposes, however, it may be duller in appearance than desired. A bright smooth uniform deposit which may be more commercially desirable can be obtained by adding conventional brightening agents to the plating bath. Amoung the compounds that have shown to enhance the brightness of the deposited plate are the ions of antimony, cadmium, lead, selenium, tellurium, cobalt, nickel, and molybdenum. Ions of the precious metals such as indium, gold, and silver have shown to be effective but their cost renders them impractical. It has also been found that in addition to the metal ions mentioned above, certain organic compounds such as the aldehydes act in a cooperative manner with the metal ions to enhance the electrodeposit. Aldehydes such as anualdehyde, benzaldehyde, veratraldehyde, etc. in fact any aldehyde or compound containing a carbonyl group which is capable of producing a brightening or smoothing effect in a commerical zinc plating process, appears to be capable

of promoting brightness in the cyanide-free bath.

One of the more exciting areas of the brightner research in the cyanide-free brass is the sulfur containing organic compounds. Compounds having mercaptan groups (C-SH) and the C=S groups are very effective as auxiliary brightening agents when used in this process. These compounds have demonstrated that, with further research, it will be possible to bright brass flash over nickel using cyanide free brass.

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