Cathode Process in Nickel-cobalt Alloy Deposition from Sulfamate Electrolytes-Application to Electroforming

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Electroforming is a specialized application of electroplating for the production of finished components and unique articles that cannot be made by any other method. Sulfamate electrolytes for Ni-Co deposition form highly efficient and stable solutions, but their wide use for electroforming has been hampered by the fact that the mechanism of Ni⁺² and Co⁺² codeposition is as yet imperfectly understood. Study was made of the effect of electrolyte composition and operating conditions on the Ni-Co alloy constitution and the mechanism of its electrodeposition. It was shown that the Faradaic efficiency of the deposition is characterized by a complicated dependence on pH with a maximum of 98.5 percent at pH 3.5 to 3.8. The concentration of cobalt in the deposit decreases by as much as five to seven percent for a pH rise from 2 to 5.2. A minor increase of cobalt concentration in the electrolyte is followed by a steep rise in the cobalt content of the alloy. At a ratio of cobalt to nickel of 0.1, the alloy contains 45 percent cobalt; at equal cation concentrations, the alloy contains 73 percent Co. This is because of the faster kinetics of Co⁺² reduction. By rotating-disk-electrode and chronopotentiometric methods, it was demonstrated that the rate-determining step of alloy deposition is the electrochemical reaction, complicated by adsorption. It is believed that the codeposition of Ni⁺² and Co⁺² is explained by the formation of heteronuclear surface complexes with sulfamate anion as the bidentate ligand. The alloy structure and physical and mechanical properties, such as hardness, internal stress, tensile strength, elongation and thermal stability were also studied. An optimum was found between alloy characteristics and operating conditions. Parts having complex shapes (molds, miniature nozzles and other electronic and aircraft components) were produced by Ni-Co electroforming.

Recent developments suggest that the engineering and electroforming applications of nickel and nickel-alloy plating are becoming increasingly important. Composite coatings, electroplated carbon/graphite fibers, electroformed molds, printed-circuit boards-these are only a few examples of nondecorative uses of nickel. Electroforming is a specialized application of the electroplating process concerned with the fabrication of complex parts and components that cannot be made by any other method. Modern applications of electroforming are diverse and may be categorized as follows: (1) tools, including molds and dies, diamond-cutting bands, (2) mesh and foil products, such as filters and razor screens; and (3) other products, such as space mirrors, metal optical parts, bellows, radar and waveguides.1-5 The possibilities for innovation in this area are far from being exhausted. Nickel-cobalt alloys are widely used for electroforming, owing to their magnetic and high tensile properties.

From a theoretical point of view, Ni-Co alloy plating is interesting, as it exhibits anomalous codeposition, that is, the less noble metal deposits preferentially to the more noble one. The standard equilibrium potentials of Ni and Co are -0.230 and -0.270 V vs. NHE, respectively. Accordingly, it would be expected, thermodynamically, that Ni, the more noble metal, would deposit preferentially; however, the reverse is found to be true. The discharge rate of the more noble component is inhibited, and this causes the appearance of the less noble component at a much higher ratio in the deposit than in the electrolyte. Anomalous codeposition of binary iron-group alloys has been widely discussed by many investigators,⁶⁻²⁰ but the mechanism is far from being understood. It was assumed that formation of the less noble metal is favored in aqueous solution and that metal hydroxides (MOH+) are the important charge-transfer species. Matulis et al.11 suggested that at pH above 4, nickel deposition occurs mainly through the discharge of NiOH⁺ ions. Dahms and Croll¹³ showed that anomalous deposition occurred when the hydrogen limiting current was exceeded. A mathematical model for anomalous codeposition of nickel-iron on a rotating disk has been developed by Hessami and Tobias.15 Sasaki and Talbot9 found that this model was unable to characterize fully either Ni-Co or Co-Fe electrodeposition. With minor changes to the hydrolysis constants, however, the model predictions greatly improve the fit for the Ni-Co results. Contrary to the results presented above, Glasstone¹² found that the potentials of Ni⁺², Co⁺² and Ni-Co deposition are pH independent and that the Ni-Co reduction potential lies between the Ni⁺² and Co⁺² potentials. A strong case can be made for the hypothesis that depolarization and overpolarization effects on alloy deposition depend on the potential of zero charge, on the state of the cations in the electric double layer and adsorbed adatoms.17-19

Deposition of Ni-Co alloys has evolved from hard, brittle deposits produced in Watts-type sulfate and chloride electrolytes to ductile deposits produced in sulfamate electrolytes. Mechanical and physical properties are determined by alloy composition, which in turn is controlled by the electrodeposition variables. Considering that Ni-Co platings in sulfamate electrolytes afford good mechanical properties at a high deposition rate (7 to 20 μ m/min), compared to Watts or chloride baths,^{2,21-27} it was of interest to estimate the possible importance of sulfamate-anion effect on the cathode process.

It is our purpose to contribute to elucidation of the effect of sulfamate electrolyte composition on the codeposition of Ni^{+2} and Co^{+2} , to investigate the mechanical properties of the alloy, and to optimize the bath composition and operating parameters for electroforming of parts having complex shapes and other components.

Experimental Procedure

Each experiment was carried out in a fresh solution. Solutions were prepared just before each experiment by dissolving the requisite amounts of the metal sulfamates in distilled, deoxygenated water. The concentration ranges studied were those normally encountered in industrial plating. Boric acid was used to adjust the pH. After each solution was transferred to the cell, it was sparged with argon for at least 30 min. An



Fig. 1—Surface pH (1) and pH bulk (2,3) vs. current density in Ni-Co sulfamate solutions (mmol): 1, 2 - Ni⁺² 1120, Co⁺² 70; H_3BO_3 328, NaCl 69; 3 - Ni⁺² 1120, Co⁺² 70, NaCl 69 at 25 °C.

argon atmosphere was maintained over the solutions to inhibit the absorption of oxygen. The nickel and cobalt content of the electrolytes was determined spectrophotometrically.

Electrodeposition experiments were performed with a three-electrode system consisting of a platinum counterelectrode, saturated silver chloride (SCE) reference electrode and a platinum rotating disk (RDE) working electrode (area $= 0.28 \text{ cm}^2$). The electrode rotation rates varied from 20 to 200 rpm. A three-compartment cell was used with the reference electrode connected to a Luggin capillary positioned in the flow field. The ohmic polarization drop did not exceed 10 to 15 mV and was taken into consideration. A potentiostat/ galvanostat was used to control the potential in the depositions. Potentiodynamic measurements were performed at a slow sweep rate of 400 mV/min. To determine partial currents of Ni⁺² and Co⁺² reduction and H₂ evolution, 7 to 10 equidistant points were selected in the overall polarization curve. Each potentiostatic electrodeposition corresponding to the chosen points was terminated after the amount of charge passed into the solution was approximately equal to rinsed with a solution consisting of a 4:2:1 volume ratio of sulfuric acid, nitric acid and water, respectively. This was followed by a thorough rinse with distilled deionized water. The platinum disk was cleaned by immersion in 0.5 M NH_2SO_3H and sweeping from -0.2 to 1.3 V for five min. Copper plates had been previously cleaned in alkaline solution, etched in 15-percent H_2SO_4 for 15-20 sec and thoroughly rinsed with distilled deionized water. The bath temperature varied from 22 to 60 ±2 °C.

The measurements of surface pH were performed galvanostatically by the use of a nickel-hydrogen reversible electrode²⁸ and calculated from Eq. (1).

$$pH_s = E/0.058$$
 (1)

where E is the electrode potential determined from potential drop curves at 0.02 sec after current interruption.

The formation of Ni⁺² and Co⁺² complexes with sulfamic acid has been studied by nuclear magnetic relaxation (NMR). The investigations were conducted over a wide range of reagent concentrations and solution acidity.

Metal distribution was studied in a 150-mL Haring-Blum cell and calculated from Eq. (2).

$$A = \log L / \log M \tag{2}$$

where L is the ratio of cathode spacing and M is the ratio of deposit weights on the near and far electrodes. According to Chin,²⁹ at ideal metal distribution, log M = 0, $A = \infty$; when there is no secondary distribution, A = 1 and, in the absence of deposit on the far electrode, A = 0.

Tensile tests were carried out at room temperature on a constant crosshead machine, type MP-05, at a speed of 3.33×10^{-5} cm/sec on 200- µm-thick samples. The deposits were electroformed nonadherently on flat stainless steel cathodes and removed mechanically, care being taken not to deform the specimens severely while removing them. Hardness was measured with a microhardness tester, using a 100-g load. Indentations were made on the 50-µm-thick deposits. Inter-

1.0 C. The actual value of the total charge accumulated was measured by a coulometer. Mechanically polished, disk copper M00 plates were used as cathodes in quantitative studies. After 50 µm-thick deposition, the samples were washed and dried. The electrodeposited alloys were analyzed for cobalt and nickel by an X-ray fluorescence method. For each set of electrodeposition conditions, duplicate or triplicate runs were performed.

Prior to each experiment, the glassware and disk were pretreated. Glassware was

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Composition of Sulfamate Electrolytes for Ni-Co Alloy Deposition

Electrolyte #	e Com n	position nmol		Co ⁺² to Ni ⁺² ratio	Total conc. of salts, mmol
	$Ni(NH_2SO_3)_2$	Co(NH ₂ S	$(\mathbf{SO}_3)_2$ $\mathbf{H}_3\mathbf{BO}_3$,
1	1155	35	328	0.032	1190
2	1120	70	328	0.062	1190
3	1083	108	328	0.1	1190
4	954	238	328	0.25	1190
5	596	594	328	1.0	1190
6	1120	70	82	0.062	1190
7	1120	70	164	0.062	1190
8	1120	70	656	0.062	1190
9	160	10	47	0.062	170
10	640	40	187	0.062	680
11	1440	90	420	0.062	1530

All electrolytes contain 69 mmol NaCl.



Fig 2a—Ni⁺² relaxation efficiency coefficient vs. Ni⁺² concentration in sulfamate solution, pH 3.1.

nal stress was measured by a Brenner-Senderoff contractometer on deposits 15 μ m thick and by X-ray diffraction on 100- μ m-thick deposits. Two X-ray pictures at primary beam angles of 0 and 50° were taken from every sample at 7-8 points. The errors of the measurements of physical and mechanical properties did not exceed \pm 5 percent. Heat-treatment of the 200- μ m-thick samples was carried out at 200, 400, 600 and 700 °C. High-temperature oxidation was detected at 600, 800 and 1000 °C on 10 hr heating.

Results and Discussion

As was shown previously,^{11,21, 30-32} electrodeposition of irongroup alloys is followed by a local pH rise near the electrode surface that is favored when H₂ is evolved simultaneously with alloy deposition. Changes in bulk pH and surface pH in Ni-Co sulfamate electrolyte (pH 3) as a function of polarization are shown in Fig. 1. Even though the accuracy of pH values obtained near the electrode is not fully satisfactory, the rise in surface pH was clearly detected. The acidity change is most pronounced at high cathode current densities. Whereas the pH in the bulk of the solution increases up to 3.4, the surface pH rose to 10 at $i = 500 \text{ A/m}^2$. It should be noted that despite the decrease in bulk and surface acidity, sulfamate electrolytes are known to be more stable with pH changes than sulfate electrolytes. In the view of Berezina,³³ this phenomenon may be explained by the possible deprotonation effect of the NH₂SO₃ anion at high pH.

Formation of Ni^{+2} and Co^{+2}

Complexes with Sulfamic Acid

The basic constituent of electrolytes under investigation was nickel sulfamate, Ni(NH2SO3), a salt of a strong monobasic sulfamic acid, NH₂SO₃H, which is similar in structure to sulfuric acid, with one hydroxyl group replaced by an amino group. A spectroscopic study of the nickel sulfamate bath was undertaken by Krishnaswamy,³⁴ and the formation of Ni sulfamate complexes was demonstrated. There are some discrepancies between these results and research data reported by Berezina et al.,33 who indicated the absence of Ni+2 complexes in sulfamate solutions. It was therefore of interest to study the possibility of complexation reactions of Co⁺² and Ni⁺² with sulfamic acid, especially at high reagent concentrations, over a wide range of solution acidity. We studied complex formation by NMR. The dependencies of the relaxation efficiency coefficient (K_{e1}) of Ni⁺² and Co⁺² on pH and concentrations of reagents are shown in Figs. 2a and 2b. As may be seen from the plots, the K_{el} for all of the solutions



Fig 2b—Ni⁺² (1, 2) and Co (3) relaxation efficiency coefficients vs. pH in sulfamate solutions (mmol): $1 - Ni^{+2} 571$, $NH_2SO_3H 1200$; $2 - Ni^{+2} 5$, $NH_2SO_3H 384$; $3 - Co^{+2} - 5.2$, $NH_2SO_3H 1200$.

under investigation is almost constant up to pH 6, indicating that there is no formation of nickel or cobalt sulfamate complexes, or that any complexes formed are weak and unstable. It is believed that there is an outer-sphere interaction mechanism between the sulfamate anion and Ni⁺² and Co⁺² through the delocalized protons of water molecules. The aquo complex of Ni⁺² has $K_{el(0)} = 650$ L/mol sec, and the rise in K_{el} above this value in strong acid solution may be associated with proton exchange between the first coordination sphere and the bulk of the solution.³⁵

Study of the Electrode Processes

Factors investigated in Ni-Co deposition included electrolyte concentration, current density, pH, temperature and surfaceactive additives. The various compositions of sulfamate electrolytes were examined and are listed in Table 1. The concentration of Ni⁺² varied from 160 to 1400 mmol; C_{Cor} was 10 to 600 mmol; $C_{H_1BO_3}$, 50 to 700 mmol. All of the solutions contained 7 mmol NaCl. Alloy films were deposited potentiostatically onto the platinum rotating disk electrode (RDE) from nickel ($C_{Ni^{+2}} = 1120$ mmol), cobalt ($C_{Co^{+2}} = 70$ mmol) and Ni-Co (#2, Table 1) sulfamate baths at pH 3.0. As the electrode rotation rate (ω) is increased, a steady rise in the current density is observed at cathode potentials over -0.7 V for Ni, Co and Ni-Co electrodeposition at 25 °C. The extrapolated i- $\omega^{1/2}$ straight line does not pass through the origin (Fig. 3). This indicates that the deposition proceeds under activation and mass transport control. Also, there is generally a deviation of the Tafel slope at high cathodic polarization. This cannot be explained by diffusion



Fig. 3—Levich plots of i vs. $\omega^{1/2}$ in nickel-cobalt sulfamate electrolyte at pH 3.1; temp 25 °C and polarization potential, V: 1 - (-0. 65), 2 - (-0.7), 3 - (-0.8), 4 - (-0.9).



Fig. 4a—Current efficiency (1, 2, 3) and Ni-Co alloy composition (4, 5) vs. bath temperature in sulfamate electrolyte #2 at pH 3.3 and current densities (A/m^2) : 1, 5-500; 2, 200; 3, 4-50.

limitations alone, inasmuch as the experimental results were obtained at a small percentage (less than 40 percent) of the limiting current for Ni, Co and Ni-Co electrodeposition. Moreover, an increase of rotation rate by a factor of eight caused the cathode current density to rise by a factor of only 1.5 to 2. It is believed that this phenomenon may be related to the preceding chemical reaction (a descending curve of

 $i\omega^{1/2}$ -i dependence) or to the formation of a film adsorbed on the electrode surface.

To study the kinetics of Ni-Co electrodeposition, the method of partial polarization curves onto a stationary electrode was used. With rise in bath temperature from 25 to 60 °C, the alloy and cobalt current efficiencies increase, while there is no noticeable change in Ni current efficiency (Fig. 4a). Within the range of current densities studied (200 to 1500 A/m²), the alloy current efficiency increases with increasing current density up to 96 percent at $i = 1000 \text{ A/m}^2$ and 25 °C. A further increase in current causes the Ni-Co current efficiency to fall to 89 percent (Fig. 4b). The cobalt content is inversely proportional to the applied current density over all temperature and pH ranges under investigation.

Changes in partial current efficiencies are usually more pronounced with acidity variations. The plots of alloy and component current efficiencies go through a maximum in the vicinity of pH 3.3 (Fig. 5). With increase in pH from 2 to 3.3, cathodic polarization of Ni-Co deposition decreases. The curves shifted toward a more positive value and the rate of Co⁺² and Ni⁺² reduction became 1.4 and 1.6 times as great, respectively, as at pH 2. In acid solutions, the discharge of H_2O^+ proceeds simultaneously with iron-groupmetal deposition. Once the local pH near the electrode surface is about 7, hydrogen evolution can take place by the reduction of water molecules. The activation energy of this process is 9 kcal/mol greater than for H₂O⁺ reduction, and this is responsible for the increase in the partial efficiencies of nickel and cobalt and decrease of cathodic polarization.



Fig. 4b—Ni-Co alloy current efficiency vs. current density in sulfamate electrolyte #2 at pH 3.3 and bath temperatures, °C: 1-55; 2-25.

On the other hand, at pH 4.5-5 the formation of electrochemically inactive complexes, such as $M(OH)_2 (H_2O)_{n-2}$ in the vicinity of the cathode is one of the reasons for the lower current efficiency of the alloy.

The quality of deposits at pH bulk lower than 2.0 was unacceptable because rapid hydrogen evolution interfered with regular crystal growth, resulting in porous and dull



Fig. 5—Current efficiency and composition of the Ni-Co alloy vs. pH in electrolyte #2 at 55 °C and i (A/dm²): 1- 50, 2- 200, 3- 500.



Fig. 6— Co^{+2} , (1, 2), N^{+2} (4, 5), Ni-Co alloy current efficiency (7, 8) and cobalt content (3, 6) vs. total cation concentration in sulfamate electrolytes # 9, 2, 10, 11 at pH 3.3 and 55 °C

Table 2 Matrix of Experiment Design

\mathbf{X}_{1}	X_2	X ₃	$_{1}y_{1}$	₂ y ₁	₃ y ₁	$_{1}y_{2}$	₂ y ₂	₃ Y ₂	${}_{1}y_{3}$	₂ y ₃	₃ y ₃	$_{1}y_{4}$	₂ y ₄	₃ Y ₄
Co:Ni	i _c	pН	$\boldsymbol{H}_{\!\boldsymbol{\mu}\!\boldsymbol{l}}$	$H_{\mu 2}$	$H_{\mu 3}$	$\sigma_{_{1}}$	σ_{2}	$\sigma_{_3}$	$\sigma_{_{in1}}$	$\sigma_{_{in2}}$	$\sigma_{_{in3}}$	CE1	CE2	CE3
0.025	200	2.2	2.8	2.9	3.08	0.76	0.80	0.73	60	61	60	81	83	81
0.06	200 800	2.2 2.2	3.30 2.61	5.18 2.58	5.42 2.50	0.91	0.87	0.90 0.69	58 75	60 73	57 73	85 91	80 92	87 90
$0.06 \\ 0.025$	800 200	2.2 5.1	2.88 3.68	3.1 3.80	3.1 3.68	$0.84 \\ 0.70$	0.83 0.65	0.76 0.66	72 100	70 98	69 101	93 86	93 87	94 86
0.025	200	5.1	3.93	3.94	4.20	0.92	0.85	0.82	100	102	96	91	91	89
$0.025 \\ 0.06$	800 800	5.1 5.1	3.38 3.44	3.09 3.70	3.26 3.60	0.81 0.74	0.83 0.77	$0.82 \\ 0.75$	135 140	130 135	139 132	81 82.8	79 84	83 80

 Y_1 - microhardness (Hµ), GPa

 Y_2 - tensile strength (σ), GPa

 Y_3 - internal stress (σ_{in}), MPa

 Y_{4} - alloy current efficiency (CE), %

X₁ - cation conc. ratio in sulfamate electrolyte (Co:Ni)

 X_2 - Current density (i), A/m²

X₃ - pH

Regression equations

$$\begin{split} y_1 &= 3.3 + 0.18X_1 - 0.19X_2 + 0.34X_3 \\ y_2 &= 0.78 + 0.05X_1 - 0.018X_2 - 0.03X_1X_2 - 0.02X_1X_3 + 0.028X_2X_3 \\ y_3 &= 91.5 + 12X_2 - 25.7X_3 + 5.8X_2X_3 \\ y_4 &= 86.5 + 1.47X_1 - 1.58X_3 - 0.58X_1X_2 - 3.7X_2X_3 \\ H\mu &= 3.9 \text{ GPa}, \sigma = 0.9 \text{ GPa}, \sigma_{\text{in}} = 75 \text{ MPa}, \text{CE} = 94\%, \\ \text{Conc. Co:conc. Ni} &= 0.06, \text{ i} = 250 \text{ A/m}^2, \text{ pH } 3.95 \end{split}$$

deposits. At pH bulk higher than 4.5, powdery deposits were observed. The maximum in alloy current efficiency at pH 3.3 correlates well with low internal stress, as observed by Greene²⁴ for Ni sulfamate electrolytes and, as we have found (see Table 2). The cobalt content in the alloy diminishes to 5-7 percent only with the drop of sulfamate solution acidity from pH 2 to 5.1. It should be emphasized that the order of the cathodic reactions of Ni⁺² and Co⁺² with respect to OH⁻ was found to be close to zero (n~0.2).

As the net concentration of the cations increases, the alloy becomes enriched with cobalt, the concentration of which rises from 10 to 32 wt pct (Fig. 6). This effect is more pronounced at low current densities. Cathodic polarization of alloy deposition decreases substantially when the net cation concentration is varied from 170 to 1530 mmol (electrolytes #2, 9-11, Table 1). At a cathode potential of 0.6 V vs. SCE, Co, and this factor received our primary consideration. From Fig. 7, it is obvious that the content of cobalt is always higher than that

content of cobalt is always higher than that expected from the cobalt concentration in the bath. At a ratio of 0.1, the deposit contained 45 percent cobalt, while at a ratio of 1.0, the cobalt content was 73 percent. Consequently, for Ni-Co alloys, there is an unambiguous indication of the inhibition of deposition of the more noble metal and promotion of the deposition of the less noble metal. The data are in good agreement with other investigators.^{1,2,12,36} The alloy current efficiency reaches a maximum at a cobalt to nickel concentration ratio in the electrolyte equal to 1:16, which corresponds to 22-28 percent of cobalt content in the alloy. The maximum of the current efficiency is coincident with the formation of the more sophisticated structure of Ni-Co alloy. Further decrease of current efficiency as a function of Co+2 concentration in a sulfamate electrolyte may be attributed to the decrease in hydrogen evolution overpotential for the cobalt-rich alloys. Partial polarization curves of

the rate of Co+2 and Ni+2 reduction increased

als can best be appreciated from study of the effect on alloy deposition of the ratio of Ni to

The anomalous behavior of iron-group met-

by factors of 18 and 6, respectively.

 Ni^{+2} and CO^{+2} codeposition are shown in Fig. 8a,b. It was found that change of temperature and sulfamate bath composition does not influence the Tafel slope, which is $120 \pm 5 \text{ mV}$ and $112 \pm 5 \text{ mV}$ for Co^{+2} and Ni^{+2} reduction, respectively. From Tafel slope values, it is expected that Ni-Co alloy deposition is a two-stage process, where the rate determining step is a gaining of the first electron. An additional support for this assumption is the large apparent activation energy of alloy deposition (17.2 kcal/mol). The cathode reactions were found to be of the first order with respect to Ni^{+2} and Co^{+2} concentrations.

Curves of potential drop following current interruption were investigated to clear up the mechanism of Ni-Co deposition. The long vertical portion on the potential vs. time curve observed after current interruption may be attributed to a high degree of activation limitation of the reaction (the ohmic polarization in all sulfamate electrolytes under investigation did not exceed 10 mV). In addition, the constant-potential segment occurs on the potential drop curves. This can be explained by the formation of an adsorbed film on the electrode surface. The length of the constant potential step increases with the increase of polarization time, but does not depend on the cathode potential change from -0.5 to -1.1 V (Fig. 9). We assume the possibility of adsorption on the electrode of complexes, such as Ni(H₂O)⁺²_n, Co(H₂O)⁺²_n, Ni(OH)(H₂O)⁺_{n-1}, Co(OH)(H₂O)⁺_{n-1}. The effect of adsorption of metal hydroxides was investigated by Watson,6 Grande and Talbot,7 Andriacos et al.,8 Sasaki and Talbot,9 and Vagramyan and Fatueva,10 as well as by Glasstone and Symes,¹² Dahms and Croll,¹³ Matlosz,14 Hessami and Tobias,15 and Harris and Clair.¹⁶ Previous studies of the elemental electrodeposition of nickel,^{11,37-39} iron,^{17,38} and cobalt³⁹ have suggested the monohydroxides as the chargetransfer species. The recent model of anomalous

codeposition of Ni-Fe proposed by Matlosz¹⁴ focused on competitive adsorption effects by means of a two-step reduction mechanism for a single-metal deposition. As was shown by Berezina,³³ however, and taking account of the approximately zero order of the cathodic reaction of Ni-Co deposition with respect to OH⁻ concentration, it is believed that



Fig. 8a. Partial polarization curves of Co^{+2} reduction in sulfamate electrolytes 1-4 at pH 3.3 and temp = 55 °C.



Fig. 8b—Partial polarization curves of Ni^{+2} reduction in sulfamate electrolytes 1-4 at pH 3.3 and temp 55 °C.



Fig. 7—Current efficiency (1, 2) and Ni-Co alloy composition (3, 4) vs. cobalt-tonickel ion conc. ratio in sulfamate electrolyte at pH 3.3, temp 55 °C and current density, A/m^2 : 2, 4-200; 1, 3-500.

hydroxyl anions are not involved in the electrochemical reaction in sulfamate electrolytes, but that they can affect the outer-sphere Ni⁺² and C⁺² aquo complexes. The effect of sulfamate anions would be analogous. The hydration energy of NH₂SO₃⁻¹ is lower than that of SO₄⁻² and its radius is smaller. Accordingly, it has a higher ion potential, so solutions of

sulfamic acid have high ionic conductivity.⁴⁰ Moreover, the possibility of adsorption of sulfamate anions on the electrode surface cannot be ruled out. We believe that this phenomenon may be associated with:

1. The effective positive charge of aminogroup protons of the NH₂SO₃⁻ anion;

2. The adsorption of aqua complexes of $Ni^{\scriptscriptstyle +2}$ and $Co^{\scriptscriptstyle +2}$ on the electrode.

The presence of three electron-donating centers (atoms of oxygen) in the sulfamate anion would lead to a decrease in repulsion of the positively charged Ni⁺² and Co⁺² aquo complexes by decoordination of water molecules and their substitution by bridging through $NH_2SO_3^-$. In such a situation, the sulfamate anion would act as a bidentate ligand. The generated binuclear complex would be positively charged and may readily interact with the electrode surface. An increase in cathodic polarization would be followed by an increase in the concentration of surface bidentate complexes and by the subsequent formation of a hetero-polynuclear complex, and can be attributed to the chemical reaction preceding the electrochemical reduction. It is thought that the formation of such a complex would be favorable for the electrodeposition of Ni-Co alloy in sulfamate electrolytes. The presence of sulfur in the deposit is good indirect evidence of sulfamate anion involvement in the cathodic reaction. The adsorption of sulfamate anion and the presence of sulfur



Fig. 9a—Length of the horizontal segment of the potential drop curves vs. polarization potential in sulfamate electrolyte #2 at 25 $^{\circ}$ C.



Fig. 9b—Length of the horizontal segment of the potential drop curves vs. polarization time in sulfamate electrolyte #2 at 25 $^{\circ}$ C.

in Ni and Ni-Co platings was determined by Semyenova *et al.*³⁶ Auger electron spectroscopy experiments performed by Dini and Johnson,⁴¹ showed that the sulfur content is about 10 ppm and it is extremely mobile in the grain boundaries of electrodeposited nickel. Also noteworthy are the higher-order deposition rates in sulfamate electrolytes and fine crystals of Ni-Co alloy, as compared to platings from sulfate and chloride baths.

To explain the anomalous codeposition of Ni⁺² and Co⁺², let us consider the individual complexes from the stand-

point of crystal-field theory. In the light of this theory, Ni^{+2} and Co^{+2} , complexes can be related to coordinative substances, the structures of which show little sublevel splitting, that is, high-spin complexes are more typical and would explain the preferential reduction of Co^{+2} , compared with Ni^{+2} , resulting in a considerable excess of cobalt in the alloy (see Fig. 7). Moreover, high-spin complexes involved in the reaction would permit a two-step reduction mechanism, which is in complete agreement with the experimental Tafel slopes.

Fig. 10 — Optical micrographs of Ni-Co alloy: (a) as deposited; (b) annealed at 600 °C for 1 hr.

Structure, Physical &

Mechanical Properties of Ni–Co Alloys The physical and mechanical properties of the deposits, the maximum allowable current density and electrolyte stability are used as basic guidelines in deciding which type of electrolyte to employ. There are additional demands, such as uniform distribution of current and metal over the cathode surface and absence of dendrite formation, in the case of electroforming of parts having complex shapes. As was previously shown, the maximum current efficiency (98.5 percent) of Ni-Co alloy deposition was achieved in sulfamate electrolytes at pH close to 3.3. At pH 2.2 and 5.1, the alloy current efficiency was 92.3 and 80.8 percent, respectively (i = 500 A/m²).

Metal distribution in sulfamate electrolytes, calculated from Eq. (2) changes in a similar way, reaching 0.94 at pH 3.3. Higher bath temperature and a decrease in current density to 200 A/m² and total cation concentration to 800 mmol was followed by an improved logarithmic distribution index of 1.2. It was found that all the 30- μ m-thick deposits were practically non-porous.

The correlation of deposition parameters with microstructural features and mechanical properties is an important undertaking. The deposited Ni-Co alloy containing 20 percent Co, appears to consist of a large number of layers, as indicated in the optical (440X) micrograph (Fig. 10). The most likely explanation for these striations is that they represent minor composition gradients. The annealing of specimens in vacuum for two hr at 200 °C gives rise to a homogeneous, columnar structure typical of nickel. Well-shaped cuboid particles were observed in the deposits by X-ray diffraction. Alloys, composed of 2 to 40 percent Co exhibited a preferred (110) crystal growth orientation. The increase of cobalt content

growth orientation. The increase of cobalt content from 2 to 40 percent was followed by an increase in the lattice parameter from 3.524 to 3.620 Å and a change of the angle of texture de-orientation from 8 to 25°. It should be mentioned that the angle of texture de-orientation of the alloy containing 20 percent cobalt, is only 11°, suggesting very sophisticated (highly ordered) alloy structure.

Hardness is known to be a structure-sensitive property. The microhardness values were affected mainly by the ratio of concentration of cobalt to nickel, and by the pH of the sulfamate electrolyte. The plot of alloy microhardness vs.



b



Fig. 12-Tensile strength (1) and ductility (2) vs. Ni-Co alloy composition.

alloy composition is shown in Fig. 11. This behavior suggests the formation of a single-phase solid solution on Ni-Co alloy deposition. The hardness of the alloy decreased slightly when annealed at 200 $^{\circ}$ C and the effect became marked only above 650 $^{\circ}$ C.

Many failures of electroplated and electroformed parts have been attributed to the presence of highly compressive or tensile stress in the deposit. High internal stress may cause loss of corrosion protective properties, as shown by the occurrence of cracking and enlargement of pores, flaking of the deposit and consequent loss of fatigue strength. High internal tensile stress may also cause warping or distortion of the electroform after separation from the mandrel. Internal stress in nickel and nickel-cobalt deposits may result from the deposition conditions, from the presence of organic and inorganic impurities and even from the method of stress testing. Precise agreement of data from different sources cannot, therefore, be expected. In this study, the effect of the operating conditions on internal stress was studied. It was found that the initially strong tensile internal stress rapidly diminished as the thickness increased, reaching a substantially constant value at a thickness of 15 to 25 µm. There was little variation of internal stress values with current-density changes for both Ni and Ni-Co (5 percent Co) deposits. It ranged from 4.2 to 5.6 kg/mm² for Ni, compared with 7 to 8.4 kg/mm² tensile stress for Ni-Co.² A fairly direct correlation was found between pH of the low-cobalt-concentration electrolytes and internal stress of the deposit (see Table 2). It should be mentioned, however, that in high-cobalt-concentration solutions, the internal stress of the alloy depends strongly on cobalt content.

Strength characteristics are mainly dependent on alloy composition. Tensile strength increases almost linearly with increase in Co content, reaching 1.5 GPa, while the alloy ductility decreases (Fig. 12). It was found that Ni-Co alloys, containing as much as 50 percent Co are high-strength ductile deposits that can be easily separated from the stainless steel base. This is of prime importance for electroforming. Further increase of cobalt content is followed by alloy embrittlement.

To estimate the effect of operating conditions on the microhardness, tensile strength, internal stress and rate of alloy deposition, a statistical technique known as factorial experiment design was used. Experimental results are shown in Table 2. The mathematical simulation is represented by four regression equations that show that the alloy properties are affected by a compound interaction of several operating parameters. The most significant factors are pH, current density, and the cobalt-to-nickel ratio in the sulfamate electrolyte. Optimum operating conditions for Ni-Co alloy electrodeposition were experimentally established. For instance, for maximum hardness of the alloy, the cobalt-to-nickel ratio should be 0.06, the cathode current density 250 A/m², and pH 3.9. With these operating parameters, the alloy will deposit with a current efficiency of 94 percent. Its hardness will be 3.95 GPa, tensile strength 0.9 GPa and internal stress 75 MPa.

High-temperature alloy oxidation at 600, 800 and 1000 °C was found to be 0.03, 0.5 and 1.2 mg/cm² hr, respectively. The thermal expansion coefficient of an alloy containing 30 percent Co was 9.5 x 10⁻⁶/deg, close to the thermal expansion coefficient of platinum. Such

properties permit the use of the alloy in thermocouples. Using the recommended electrolyte composition and optimal operating conditions for low internal stress, high tensile Ni-Co alloy deposition, a number of parts having complex shapes were fabricated. High-precision micronozzles, 12 to 30 mm long, with irregular inner shapes and 0.1 mm outlet diameter were successfully made. The nozzles, which maintained accurate control of a fuel jet, were used for thrust rocket engines and for hydraulic amplifiers. Electroformed corrosion and wear-resistant protective articles having a "Vshaped" section and 300-1500 mm length, increased the service life of screws and helicopter propellers by a factor of 1.5-2. Nickel-cobalt molds with a highly lustrous finish have been made for special medical functions for a manufacturer of plastic components. The molds can withstand more than 3,000 high-quality castings.

Findings

- 1. The ratio of cobalt to nickel in the deposits was always higher than that in the bath, indicating preferential deposition of cobalt.
- The alloy composition was mainly affected by the variation in cobalt concentration, total cation content in the bath and, to some extent, by the current density and pH of the electrolyte.
- 3. The cathode current efficiency increased steadily with current density and temperature, and sharply with pH, reaching a maximum of 98.5 percent at $i = 500 \text{ A/m}^2$, pH 3.3-3.5 and temp 55 °C.

- 4. An optimal combination of physical and mechanical alloy properties, such as microhardness, internal stress, tensile strength and operating conditions was found. Complexshaped parts (molds, miniature nozzles and other electronic and aircraft components) were produced by Ni-Co electroforming.
- 5. The deposits were uniform and had a lamellar structure. Xray studies show the formation of a solid solution and an fcc structure.

Conclusions

- 1. Relying on our experiments, it is suggested that the codeposition of nickel-cobalt alloy in sulfamate electrolytes is based on competitive effects of adsorption of Ni and Co aqua complexes and sulfamate anion, with the formation of a surface hetero-polynuclear complex, where the $NH_2SO_3^-$ anion plays the role of the bidentate ligand. A two-step reduction mechanism was proved.
- 2. We believe that the anomalous codeposition of Ni-Co alloy may be explained in terms of crystal-field theory by the preferential reduction of high-spin Co⁺² cation.

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