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Bureau of Mines Report of Investigations/1985

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By J. L. Holman and L. A. Neumeier



UNITED STATES DEPARTMENT OF THE INTERIOR



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BUREAU OF MINES
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Library of Congress Cataloging in Publication Data :

Holman, J. L. (James L.)

Deposition of nickel-cobalt alloys by controlled-potential electrolysis.

(Report of investigations / United States Department of the Interior,
Bureau of Mines ; 8931)

Bibliography: p. 17.

Supt. of Docs. no.: I 28.23:8931.

1. Cobalt-nickel alloys--Recycling. 2. Scrap metals--Recycling.
3. Electrolysis. I. Neumeier, L. A. II. Title. III. Series: Report of
investigations (United States. Bureau of Mines) ; 8931.

TN23.U43 [TN798] 622s [669'.733] 84-600281

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A/dm ²	ampere per square decimeter	L	liter
A/ft ²	ampere per square foot	lb	pound
°C	degree Celsius	lb/yr	pound per year
cm	centimeter	mL	milliliter
g	gram	pct	percent
g/L	gram per liter	V	volt
h	hour	wt pct	weight percent

DEPOSITION OF NICKEL-COBALT ALLOYS BY CONTROLLED-POTENTIAL ELECTROLYSIS

By J. L. Holman¹ and L. A. Neumeier²

ABSTRACT

The Bureau of Mines is conducting research to improve technology for the recovery of strategic and critical metals, such as cobalt, nickel, and chromium, that are lost in bulk and particulate superalloy-type scrap because it has not been possible to process mixed contaminated scrap efficiently. The research approach involves melting and casting mixed superalloy scrap into soluble anodes for electrodeposition of Ni-Co alloys by controlled-potential electrolysis. The initial experimental results described in this report are from electrolytic tests using alloy anodes cast from elemental nickel, cobalt, and chromium, the main constituent metals of superalloys. Baseline data and operating parameters are necessary for Ni-Co and Ni-Co-Cr alloys before detailed experiments can be conducted on the more complex superalloy scrap. This basic research assessed the effects of cathode potential, SO₄:Cl electrolyte ratio, electrolyte pH, stirring rate, deposition time, cathode current density, and chromium concentration on cathode current efficiency, alloy deposit composition, and deposition potential at a cell temperature of 55° C.

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INTRODUCTION

As part of the goal to devise technology that provides the United States the means to meet its strategic and critical mineral and metal needs, the Bureau of Mines has been investigating procedures to recover nickel, cobalt, chromium, and other values from mixed contaminated superalloy-type scrap. Development of improved recycling technology is one of the options available to reduce high reliance on foreign sources for these metals.

A comprehensive study of the domestic availability of chromium and related critical metals contained in six classes of superalloy scrap material (1)³ revealed that over 100 million lb/yr of mixed contaminated superalloy and associated heat- and corrosion-resistant high-alloy scrap are downgraded or exported. This scrap contains over 20 million lb of potentially recoverable chromium, 5 million lb of cobalt, and 50 million lb of nickel, plus several million pounds of other alloying elements.

Superalloys and related specialty alloys, which comprise the single largest use category for cobalt, have perhaps the most stringent specifications of any alloy group. This stems from their use for jet engine and other high-reliance components where there is little margin for error. Producers will not, therefore, charge any scrap materials into melts that do not meet their specific charge specifications. Because of these requirements, mixed contaminated superalloy-type scrap is commonly reprocessed by secondary metal refiners and downgraded in use as nickel-enriched feedstock for stainless steel, cast iron, or alloy steels.

The second largest domestic use of cobalt is in the production of permanent

magnets (e.g., Alnico⁴ alloys). Substantial amounts of grinding sludge are generated in magnet manufacture, which are mostly exported for processing. A pyrometallurgical process for reclaiming Co-Ni and other values from contaminated magnet alloy grinding sludge has been investigated and patented (2). The process includes initial degreasing and elemental sulfur removal by washing in hot perchloroethylene, screening to remove grinding media, then oxidation roasting in air, and hydrogen reduction. The resulting powder product has low enough sulfur and carbon levels to be a candidate material for addition directly to permanent magnet alloy melts.

A number of processes for recycling of nickel- and cobalt-base alloys or separation and recovery of specific constituents have been investigated, but only a limited number have been used commercially.

Kusik (3) investigated a scheme for melt oxidation whereby chromium and iron from stainless scrap were oxidized to the slag for subsequent reduction to ferrochromium; earlier Bureau research had demonstrated chromium removal from superalloy scrap by melt oxidation (4). The research of deBarbadillo led to a combined pyrometallurgical-hydrometallurgical procedure (5) whereby superalloy scrap was oxidized and sulfidized under controlled conditions; chromium sulfide was roasted and reduced aluminothermally, and cobalt and nickel sulfides were leached, solvent-extracted, and electro-won individually. Substantial Bureau research was conducted on superalloy reclamation in the 1960's using a variety of constant-current electrodeposition and hydrometallurgy techniques (6-7).

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

⁴Reference to specific products does not imply endorsement by the Bureau of Mines.

The current investigation involves a combined pyrometallurgical and electrometallurgical approach. The Ni-Co-bearing material is melted and cast into anodes, which are then dissolved in acid sulfate-chloride electrolyte while the potential between the cathode and a reference electrode is controlled to selectively deposit Ni-Co alloy. Controlled-potential electrolysis has been used in the past primarily as an analytical tool and has not been developed for commercial selective electrodeposition of metals and alloys. The controlled potential is related to the fact that different metals ideally exhibit different reduction potentials. Standard reduction potentials are shown in table 1 for selected metals, including those commonly present in superalloys.

TABLE 1. - Selected standard reduction potentials (E_o)¹

<u>Cathode reaction</u>	<u>E_o, V</u>
$\text{Cu}^{2+} + 2e = \text{Cu}$	+0.337
$\text{Mo}^{3+} + 3e = \text{Mo}$	-.20
$\text{Ni}^{2+} + 2e = \text{Ni}$	-.250
$\text{Co}^{2+} + 2e = \text{Co}$	-.277
$\text{Fe}^{2+} + 2e = \text{Fe}$	-.440
$\text{Cr}^{3+} + 3e = \text{Cr}$	-.744

¹Reference N.H.E. (normal hydrogen electrode) = 0.

The standard reduction potentials for individual metals are derived for highly

idealized and controlled conditions not realized in actual practice for combinations of metals and variations of electrolyte ions, pH, etc. Factors such as overvoltage, passivity, electrolyte composition, temperature, etc., lead to shifts in potential and to anomalous behavior.

A main goal of this research is to devise technology for the recovery of Ni-Co alloy by electrolysis of anodes cast from superalloy scrap. This initial report describes results obtained from basic research experiments performed on alloy anodes cast from elemental nickel, cobalt, and chromium. It was deemed necessary to obtain baseline data and operating parameters on these primary elements as a requisite for extending the research to the more complex superalloy scrap.

In another phase of the research, to be described in a subsequent report, controlled melt oxidation and related refining treatments are being assessed as a potential means for pyrometallurgically removing, during the melting of anodes, part of the contained chromium, molybdenum, titanium, columbium (niobium), and other reactive metals found in superalloy scrap. Techniques are under investigation for recovery of these elements from the resultant slag.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Binary (70 Ni-30 Co) and ternary (55 Ni-25 Co-20 Cr) anodes were prepared by melting elemental nickel and cobalt of 99.9+ pct purity, and chromium of 99.4+ pct purity, in a MgO crucible in a vacuum-induction furnace under a partial pressure of helium. The temperature was taken to about 1,600° C for a sufficient period to completely alloy the component metals, as confirmed by subsequent chemical analysis. The molten alloys were poured into a preheated low-carbon steel book mold onto which a zirconia wash had been applied. The cast slab, about 1.6

cm thick, was then hot-rolled into sheet of about 0.5-cm thickness and cut into individual anodes. The cast alloys were hot-rolled for experimental convenience, to obtain an anode thickness appropriate for the 1-L cell; for larger cells, the cast thickness would suffice.

Two heats of ternary alloy with carbon additions (52 Ni-25 Co-19 Cr-4 C) were made for a few experiments. The Ni-Co-Cr alloy was melted in a small electric arc furnace. The coke breeze (carbon addition) was stirred into the melt, which

was then cast into a conical carbon mold to which a wash had been applied. This material was then remelted and cast into anodes in the vacuum-induction furnace.

Electrolytic experiments were conducted in a 1-L glass cell (fig. 1) at an electrolyte volume of approximately 900 mL. The cell temperature was maintained at $55 \pm 1^\circ \text{C}$ with a constant-temperature circulating bath. This temperature was chosen based on the work reported by Hayashi (6). Agitation in the cell was provided by a magnetic stirrer.

A single titanium cathode, 4 by 15 by 0.086 cm, was used for each electrolytic experiment. The anodes were 4 by 15 by 0.5 cm. Singular anodes were used on short-term, <8-h tests, and dual anodes, with one cathode, were used for tests extending to 24 h. The electrodes were spaced approximately 3.8 cm apart.

A saturated calomel reference electrode (SCE) was situated in a glass reservoir connected to a Luggin capillary

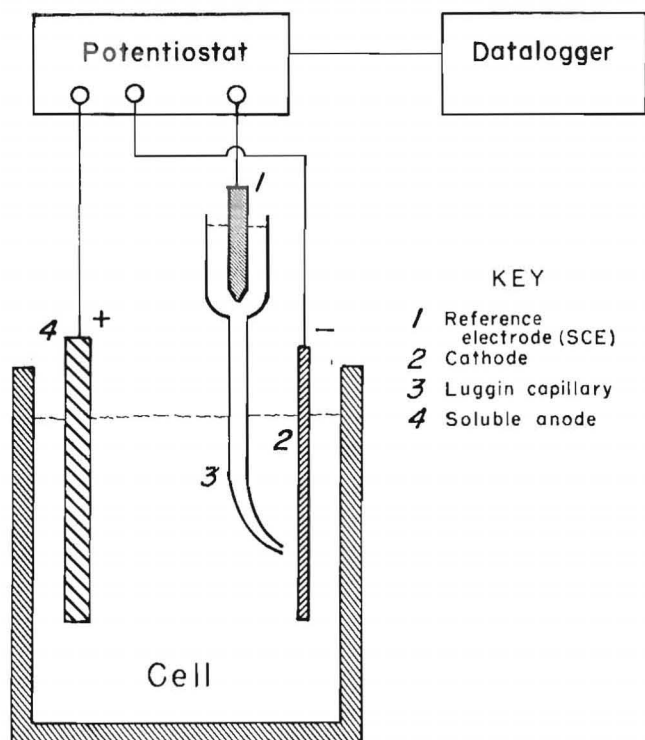


FIGURE 1. - Simplified schematic of apparatus for controlled-potential electrolysis.

containing the same electrolyte as the starting solution in the cell. The capillary tip was positioned approximately 0.3 cm from the face of the cathode. The cathode potential was controlled at specific values by a potentiostat via the reference electrode. The pH of the cell was monitored during some tests and maintained in the range of 1.0 to 1.5 by means of a peristaltic pump, controlled by a datalogger relay, that added an acid solution of predetermined $\text{SO}_4:\text{Cl}$ ratio. Measurements such as cell amperage, voltage, ampere hour, and temperature were monitored and logged automatically on the datalogger (fig. 2).

Synthetic electrolytes were prepared by dissolving certified-grade $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in distilled water and adjusting the pH with 10-pct- H_2SO_4 solution. Unless otherwise stated, the normal parameters were (1) initial electrolyte content⁵ of 45 g/L Ni, 6.5 g/L Co, 34 g/L SO_4 , and 42 g/L Cl, (2) initial pH of electrolyte adjusted to 1.0, (3) temperature of $55 \pm 1^\circ \text{C}$, (4) current density (CD) of 20 to 50 A/ft^2 ($1 \text{ A}/\text{ft}^2 = 9.29 \text{ A}/\text{dm}^2$), and (5) controlled cathode potential versus SCE of -0.75 or -0.90 V. Specific electrolyte compositions and resultant Ni-Co alloy deposit compositions are given in the results section. Dependent cell variables such as cathode current efficiency (CE) were calculated from the measured data.

The cobalt contents of electrolytes and of anode materials and cathode deposits after solubilization were determined by atomic absorption of the filtrate after precipitation of the nickel by dimethylglyoxime. Nickel contents were derived using gravimetric procedures. The high concentrations of total chromium were analyzed by the oxidation-reduction

⁵The nickel and cobalt concentrations were selected to be similar to those used in prior Bureau research (6) on superalloy scrap in which constant-current electrolysis was investigated.



FIGURE 2. - Apparatus used for electrolytic experiments.

method. Lower concentration levels of total chromium were determined by atomic absorption instrumental analysis. Carbon

was determined by the combustion method. Standard gravimetric procedures were used to analyze for sulfate and chloride.

EXPERIMENTAL RESULTS AND DISCUSSION

NICKEL-COBALT ALLOY ANODE

A series of electrolysis tests was conducted at 55° C on binary alloy anodes of 70 Ni-30 Co to assess the effects of the $\text{SO}_4:\text{Cl}$ ratio in the electrolyte at an initial pH of 1.0. The pH of the electrolyte was not fixed, however, as these were short-term (1- to 8-h) tests, and the pH remained essentially in the range 1.0 to 1.3 during this period. Titanium cathodes were used; stainless steel cathodes were also tried, but it was difficult to remove the deposits when depositing at a pH of <1.5.

The starting electrolytes contained 6.5 g/L Co and 45 g/L Ni as cobaltous and nickelous sulfates and chlorides. Electrolytes having $\text{SO}_4:\text{Cl}$ ratios of 0.04, 0.80, and 5.10 were evaluated. The high-chloride electrolyte having an initial $\text{SO}_4:\text{Cl}$ ratio of 0.04 contained 2.7 g/L SO_4 and 62.1 g/L Cl, the intermediate-chloride electrolyte having a $\text{SO}_4:\text{Cl}$ ratio of 0.80 contained 34 g/L SO_4 and 42 g/L Cl, and the low-chloride (high-sulfate) electrolyte having a $\text{SO}_4:\text{Cl}$ ratio of 5.10 contained 76 g/L SO_4 and 15 g/L Cl.

Preliminary voltammetry studies on the intermediate-chloride electrolyte and electrodes indicated that the Ni-Co deposition potential (where Ni-Co deposition began) was about -0.60 V versus SCE. Electrodeposition tests for the binary anodes were conducted at cathode potentials of -0.65, -0.75, -0.90, and -1.10 V. These tests were for periods of 1 h at -1.10 V, 4 h at -0.90 V, and 8 h at potentials of -0.75 and -0.65 V, which resulted in similar ampere hour consumption.

Data for the binary anode electrolytic experiments are given in table 2, and relationships are plotted in figures 3A through 10A. The cathode CE tended to be somewhat dependent upon the electrolyte SO₄:Cl ratio (fig. 3A). The lowest cathode CE (41 pct) was obtained with the

low-chloride electrolyte. The highest cathode CE (88 to 89 pct) was obtained with the high- and intermediate-chloride electrolytes. For a given electrolyte, the cathode CE increased as the potential was changed to more negative settings.

In general, the anode CE was above 95 pct and did not vary greatly with the SO₄:Cl ratio, although somewhat more variation was noted for the low-chloride electrolyte than for the other two electrolytes.

As the cathode potential was changed to more negative values, the nickel in the deposit first decreased (fig. 4A) and then increased for the potential of -1.10 V. The low-chloride electrolyte produced the lowest nickel deposit at each potential. The cobalt in the deposits

TABLE 2. - Short-term controlled-potential electrolytic experiments

Electrolyte SO ₄ :Cl ratio	Test duration, h	Cathode data			Deposit Ni:Co ratio	Deposit composition, wt pct		
		Potential versus SCE, V	CD, A/ft ²	CE, pct		Co	Ni	Cr
70 Ni-30 Co ANODE								
0.04.....	8	-0.65	3.9	80	1.2	45.1	54.9	Nap
	8	-.75	5.1	82	1.0	49.0	51.0	Nap
	4	-.90	13.4	85	1.0	49.4	50.6	Nap
	1	-1.10	71.3	88	1.8	36.2	63.8	Nap
0.80.....	8	-.65	2.9	61	1.3	43.8	56.2	Nap
	8	-.75	13.6	76	.9	53.1	46.9	Nap
	4	-.90	23.8	89	1.1	48.0	52.0	Nap
	1	-1.10	84.5	88	2.3	29.9	70.1	Nap
5.10.....	8	-.65	1.2	41	1.0	50.6	49.4	Nap
	8	-.75	5.3	62	.8	54.9	45.1	Nap
	4	-.90	9.4	57	.7	57.3	42.7	Nap
	1	-1.10	40.3	61	1.0	49.0	51.0	Nap
55 Ni-25 Co-20 Cr ANODE								
0.04.....	8	-0.65	4.1	75	1.3	43.7	56.3	<0.03
	8	-.75	13.2	85	1.1	47.1	52.1	.75
	4	-.90	43.5	85	1.3	43.8	56.1	<.03
	1	-1.10	75.0	86	1.6	38.0	62.0	.03
0.80.....	8	-.65	2.4	72	1.3	44.1	55.8	.10
	8	-.75	8.9	77	.8	54.5	45.4	.15
	4	-.90	10.0	78	1.0	49.4	50.3	.13
	1	-1.10	61.0	80	1.6	37.9	62.0	.12
5.10.....	8	-.65	1.2	39	1.1	48.7	51.2	.08
	8	-.75	5.4	63	.7	58.9	41.0	.06
	4	-.90	22.0	65	.9	52.9	47.0	.05
	1	-1.10	39.0	61	.9	52.5	47.5	<.03

Nap Not applicable.

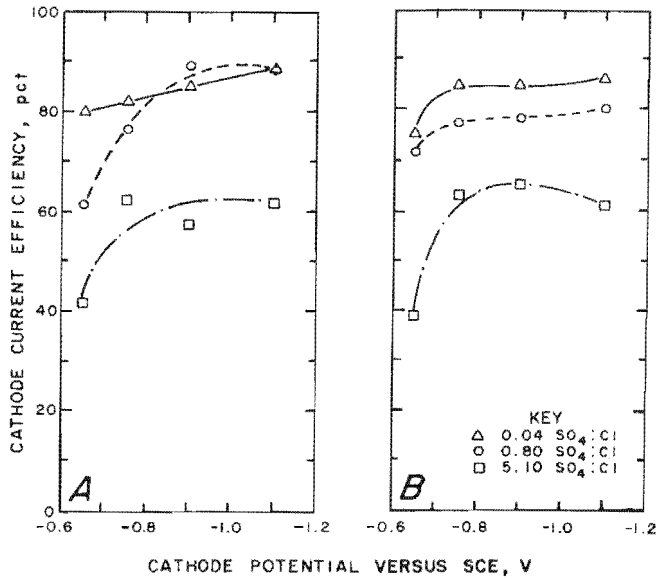


FIGURE 3. - Cathode current efficiency versus cathode potential. A, Ni-Co anode; B, Ni-Co-Cr anode.

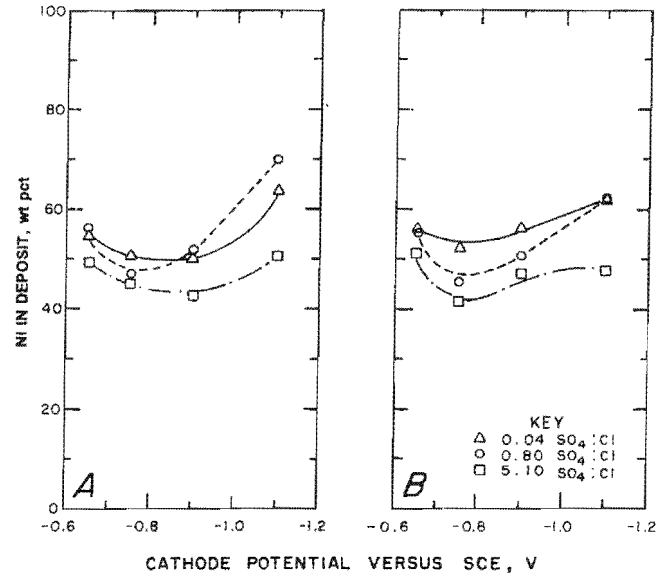


FIGURE 4. - Nickel in alloy deposit versus cathode potential. A, Ni-Co anode; B, Ni-Co-Cr anode.

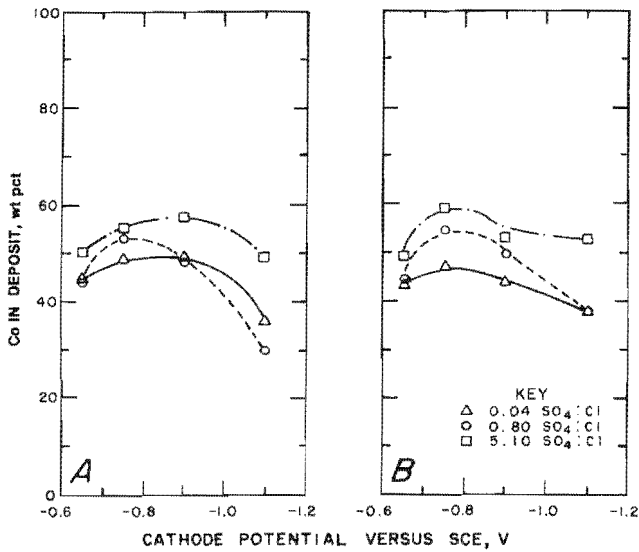


FIGURE 5. - Cobalt in alloy deposit versus cathode potential. A, Ni-Co anode; B, Ni-Co-Cr anode.

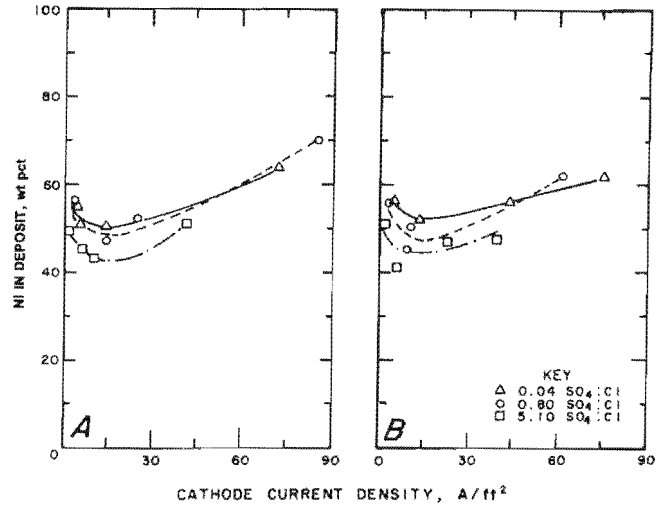


FIGURE 6. - Nickel in alloy deposit versus cathode current density. A, Ni-Co anode; B, Ni-Co-Cr anode.

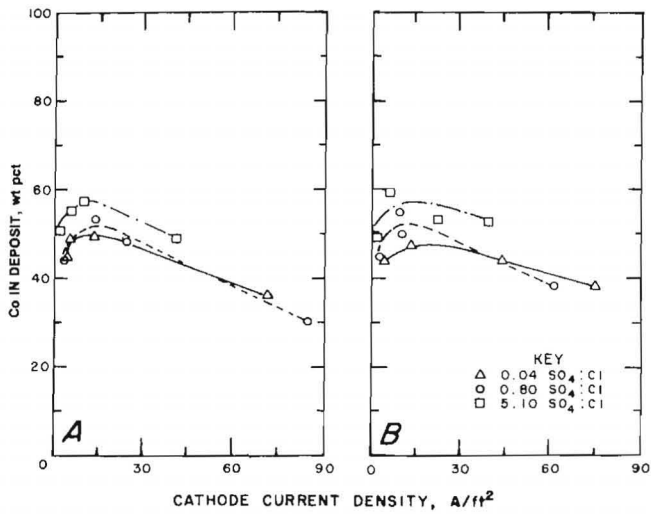


FIGURE 7. - Cobalt in alloy deposit versus cathode current density. *A*, Ni-Co anode; *B*, Ni-Co-Cr anode.

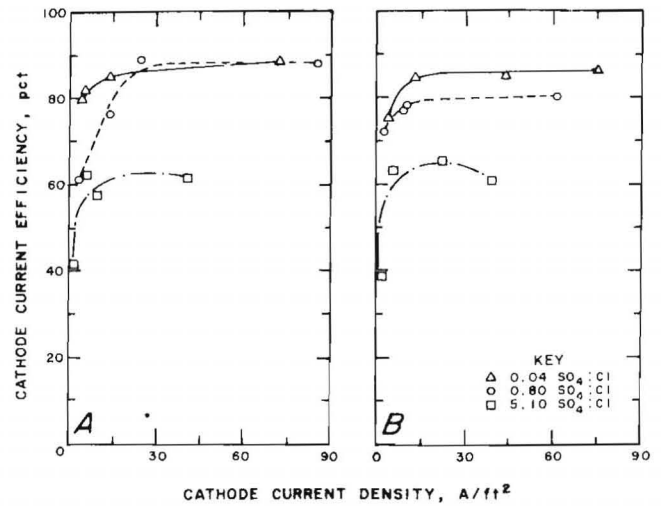


FIGURE 8. - Cathode current efficiency versus cathode current density. *A*, Ni-Co anode; *B*, Ni-Co-Cr anode.

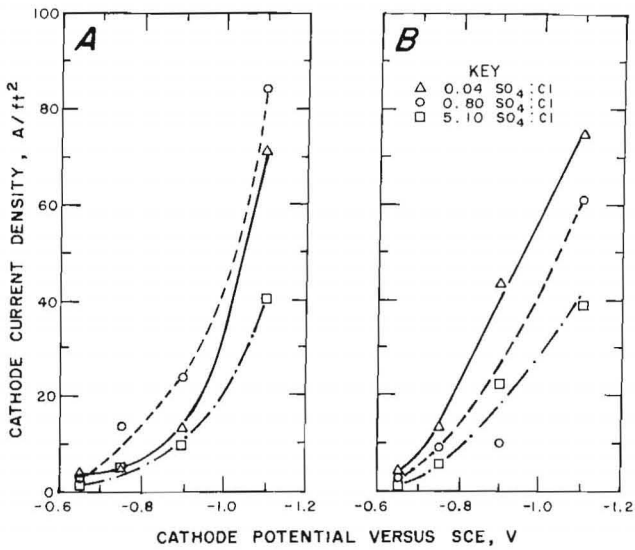


FIGURE 9. - Cathode current density versus cathode potential. *A*, Ni-Co anode; *B*, Ni-Co-Cr anode.

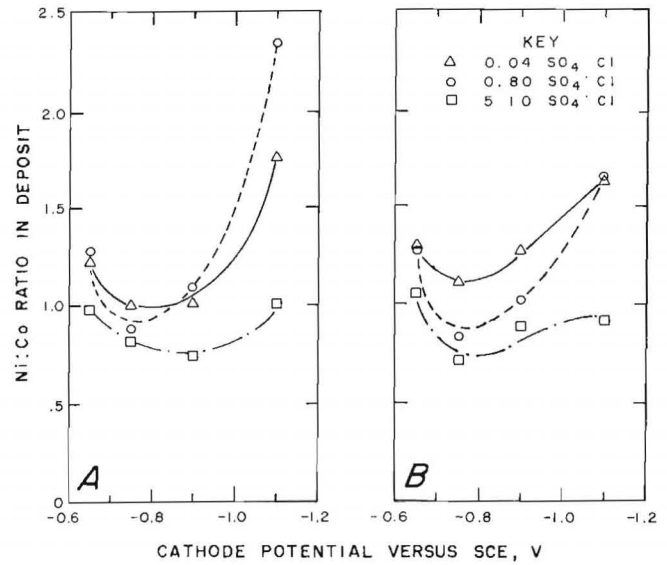


FIGURE 10. - Nickel-to-cobalt deposition ratio versus cathode potential. *A*, Ni-Co anode; *B*, Ni-Co-Cr anode.

exhibited essentially the reverse behavior as a function of potential and electrolyte $\text{SO}_4:\text{Cl}$ ratio (fig. 5A).

After an initial decrease for cathode CD values below about 20 A/ft^2 , the nickel in the deposit (fig. 6A) increased with CD. Higher CD values resulted for the high- and intermediate-chloride electrolytes. Essentially the reverse behavior occurred for the cobalt in the deposit (fig. 7A) as influenced by the cathode CD and electrolyte $\text{SO}_4:\text{Cl}$ ratio.

The data plotted in figures 3A through 7A show that there is interrelation between the nickel and cobalt in the deposit, the $\text{SO}_4:\text{Cl}$ electrolyte ratio, the controlled potential, and the cathode CE and CD. It follows that the cathode CE varies as a function of electrolyte $\text{SO}_4:\text{Cl}$ ratio and cathode CD, as shown in figure 8A. The cathode CE increased with cathode CD until essentially "saturation" levels were reached. The high-chloride electrolyte produced the higher CE values below about 20 A/ft^2 ; above about 20 A/ft^2 , there was no significant difference in CE between the high- and intermediate-chloride electrolytes.

Plotting the data for cathode CD versus the cathode potential (fig. 9A) emphasizes the strong dependence of the cathode CD on potential (as was deduced from the plots in figures 4A through 7A); the cathode CD increased markedly when the cathode potential was changed from -0.65 V to increasingly more negative potential settings up to -1.10 V .

Similarly, combining the data in figures 4A and 5A and plotting the Ni:Co ratio in the deposit versus the potential (fig. 10A) emphasizes that the ratio went through minima for each of the three electrolyte $\text{SO}_4:\text{Cl}$ ratios at intermediate cathode potentials.

It should be noted that the cathode potential of -1.10 V with the high- and intermediate-chloride electrolytes produced Ni:Co deposit ratios closest to the 70:30 ratio of the binary anode. The cathode CE for these conditions was among

the highest obtained. The intermediate-chloride electrolyte produced the highest cathode CD value obtained, 84.5 A/ft^2 (table 2, figure 8A).

A few experiments conducted with electrolytes that contained no chloride addition indicated that the deposition potential shifted to a more negative value. At a cathode potential of -0.75 V , the CD was $<1 \text{ A/ft}^2$ and the cathode CE about 5 pct. The CE was about 35 pct at potentials of -0.90 and -1.10 V . Deposits at these potentials had a Ni:Co ratio of about 0.5.

The data in figures 3A to 10A indicate that cathode CD, cathode CE, and similarity of Ni:Co ratio between anode and deposit are each favored by more negative cathode potential and by electrolytes containing substantial chloride.

NICKEL-COBALT-CHROMIUM ALLOY ANODE

A series of electrolysis experiments, with conditions that duplicated those for the 70 Ni-30 Co alloy anodes, was conducted on anodes cast from 55 Ni-25 Co-20 Cr alloy. These experiments were made so that the results could be compared with the data accumulated for the binary anode tests, to determine the influence of the presence of chromium in about the same proportion as in a number of superalloys, i.e., roughly some 20 wt pct. These tests assessed the effects of the $\text{SO}_4:\text{Cl}$ ratio in the electrolyte at four different cathode potentials. The same electrolyte compositions and cathode potentials were used as for the binary anode. The cell was operated at the same temperature (55° C), stirring rate, and respective deposition periods (also varied as function of potential) as for the binary anode. Although the pH was not controlled to a specific value, it remained in the range 1.0 to 1.3 during these short-term tests. The data obtained when using the ternary anode are plotted in figures 3B through 10B adjacent to the data for the binary anode experiments and are also included as a portion of table 2.

The trends for the Ni-Co-Cr anode experiments were generally similar to those derived for the Ni-Co anode experiments, but there were differences. The cathode CE increased with increased chloride in the electrolyte (fig. 3B), as it did for the binary anode, and as the cathode potential was made more negative. There was more separation of the CE values for the high- and intermediate-chloride electrolytes at the potentials more negative than about -0.75 V.

The nickel and cobalt in the deposit tended to show minima and maxima for each electrolyte at intermediate potential settings (figs. 4B-5B), as they did for the binary anode. For the ternary anode, the nickel remained definitely higher and the cobalt lower for the high-chloride electrolyte than was evident in the binary anode experiments, where a crossover appeared to occur for the high- and intermediate-chloride electrolytes at the more negative potentials.

The trends for nickel and cobalt in the deposit as a function of cathode CD were generally the same for the ternary and binary anode experiments (figs. 6B-7B); nickel in the deposit increased at the higher CD values after exhibiting minima in the lower CD range. For the higher CD range, the deposits for the ternary anode had somewhat less nickel and more cobalt than the deposits for the binary anode. For both anode materials, the lowest nickel and highest cobalt (lowest Ni:Co ratio) occurred for the low-chloride electrolyte.

The trends for the plots of cathode CE versus cathode CD for the ternary anode (fig. 8B) were also similar to those for the binary anode, although there was more distinction between the results for the high- and intermediate-chloride electrolytes for the higher CD values. The highest CE values resulted for the high-chloride electrolyte and the lowest for the low-chloride electrolyte.

As with the Ni-Co anode, the cathode CD for the Ni-Co-Cr anode increased dramatically as the potential was moved to more

negative values (fig. 9B). In both instances, the low-chloride electrolyte produced the lowest cathode CD at most potential settings. However, the highest CD values for the ternary anode occurred for the high-chloride electrolyte, whereas the highest CD values for the binary anode were for the intermediate-chloride electrolyte. The higher chloride content of the electrolyte evidently exerts a favorable effect on the cathode CD when chromium ions are present in the electrolyte.

For the Ni-Co-Cr anode, the Ni:Co ratio in the deposit tended to increase with increasing chloride in the electrolyte (fig. 10B). As for the Ni-Co anode, each electrolyte resulted in lower Ni:Co ratios in the deposits when the potential setting was changed from -0.65 to -0.75 V. At more negative potentials, the Ni:Co ratio in the deposits increased again. The highest Ni:Co ratios in the deposits resulted for the high- and intermediate-chloride electrolytes at a potential of -1.10 V.

The Ni:Co ratio of cathode deposits made with the ternary anode (table 2) were closest to the Ni:Co ratio of the anode when the high-chloride or intermediate-chloride electrolyte and a potential of -1.10 V were used. The cathode CD and CE were highest for the high-chloride electrolyte.

Very little evidence of anodic passivation existed in these tests. Apparently, the chloride content of the electrolytes was sufficient to depassivate the anode. However, the anode CE, generally around 95 pct for the experiments with the binary anode, was a few percent less for the experiments with the ternary anode. The anodic dissolution was consistently greater than the amount of alloy deposited, showing that anodic dissolution rate was not a limiting factor in the deposition rate.

As the $\text{SO}_4:\text{Cl}$ ratio was increased (decreased chloride), the Ni-Co deposition potential shifted somewhat to a more negative value (less noble). This was

evident from the somewhat lower CD values for the low-chloride electrolyte. This was also apparent from the fact that the Ni:Co ratio in the deposit increased as the chloride content of the electrolyte increased.

The chromium buildup in the electrolyte during this short-term experimental series with the Ni-Co-Cr anode was <1.5 g/L, and generally the deposit analyzed 0.10 pct Cr or less. As it was difficult to pinpoint effects due to the chromium in the anode for these short-term tests, longer term experiments were made using selected electrolyte and operating parameters to try to isolate the effects caused by the presence of chromium.

A few ternary anode test runs were conducted using electrolytes without any chloride addition. The results were similar to those discussed earlier for comparable tests made with the binary anode. Essentially no deposit was obtained at cathode potentials less negative than -0.75 V as the CD was <0.4 A/ft². This indicates that the deposition potential had shifted in the negative direction. Even at a potential of -0.90 V, the CD was only 4 A/ft²; however, the cathode CE for tests at the two most negative cathode potentials, -0.90 and -1.10 V, was 31 and 39 pct, respectively. The Ni:Co ratios of the deposits were 0.4 and 0.6 for the cathode potentials of -0.90 and -1.10 V, respectively. With the all-sulfate electrolyte, anode dissolution was lower for the ternary anode than for the binary; cathode deposition rate then became limited by anodic dissolution rate.

EXTENDED DEPOSITION PERIODS

Longer term deposition tests were conducted at one cathode potential value (-0.90 V versus SCE) for each of the three electrolytes (SO₄:Cl = 0.04, 0.80, and 5.10) and both binary and ternary anodes (70 Ni-30 Co and 55 Ni-25 Co-20 Cr). These experiments were run for three 8-h periods in the same electrolyte, with a new titanium cathode for

each 8-h interval. The pH of the electrolyte was not controlled, although it was adjusted to 1.0 at the beginning of the 24-h test. Two anodes and one cathode were used in these tests. Results are shown in table 3.

The following observations were evident when the long-term binary and ternary anode experiments were compared: (1) The cathode CD was lower with the ternary anode, (2) metallic deposits were obtained in the binary anode tests, but partly nonmetallic deposits [probably Cr(OH)₃] were produced over the initial metallic deposit in all the ternary anode tests during the final 16 h of deposition, (3) the partly nonmetallic deposits generally analyzed 3 to 18 pct Cr, and the metallic deposit from the first 8 h with the ternary anode analyzed 0.7 and 1.2 pct Cr for the high- and low-chloride electrolytes, respectively, and (4) the pH of electrolytes during ternary anode tests did not rise above 3.3, whereas for binary anodes, the pH increased to 5.6.

For the binary anode, the Ni:Co deposit ratio increased with increased deposition period, for all three electrolytes. For the ternary anode, the Ni:Co deposit ratio was about the same in the first 8-h period (for which the deposits remained metallic) for the high- and intermediate-chloride electrolytes and lower for the low-chloride electrolyte.

As pH was thought to have a significant effect on these results, an additional 22-h test was made using a ternary anode and the intermediate-chloride electrolyte in which the pH was maintained at 1.0±0.1. All other operating parameters were the same as for the 24-h tests. The deposit remained metallic for all three depositing periods. The final 6-h deposit contained the most chromium. This deposit analyzed 0.60 pct Cr and the spent electrolyte analyzed 9 g/L Cr. Analysis of spent electrolytes from Ni-Co-Cr ternary alloy dissolution indicated that the chromium ions were present as Cr³⁺; no Cr⁶⁺ was detected.

TABLE 3. - Long-term controlled-potential electrolytic experiments at a cathode potential of -0.90 V versus SCE

Electrolyte SO ₄ :Cl ratio	Cathode data		Deposit Ni:Co ratio	Deposit composition, wt pct		
	CD, A/ft ²	CE, pct		Co	Ni	Cr
70 Ni-30 Co ANODE						
0.04.....	48	66	1.2	44.7	55.3	Nap
	76	100	2.0	33.2	66.8	Nap
	53	98	2.3	30.2	69.8	Nap
0.80.....	36	90	1.1	48.0	52.0	Nap
	46	99	1.6	38.9	61.0	Nap
	60	100	1.7	37.3	62.7	Nap
5.10.....	49	82	1.6	38.7	61.3	Nap
	25	97	1.3	43.8	56.2	Nap
	31	100	3.5	22.0	78.0	Nap
55 Ni-25 Co-20 Cr ANODE						
0.04.....	25.0	85	1.6	37.5	61.8	0.7
	2.3	NA	7.7	2.4	18.5	3.8
	6.3	NA	14.2	3.5	49.8	.9
0.80.....	22.0	100	1.7	37.1	62.0	.8
	14.0	NA	3.7	12.7	47.0	9.4
	15.0	NA	4.1	12.2	50.6	7.2
5.10.....	35.0	73	1.1	46.3	52.5	1.2
	9.0	NA	3.8	7.3	28.1	18.8
	11.0	NA	3.9	8.4	33.1	16.6
55 Ni-25 Co-20 Cr ANODE, ELECTROLYTE pH = 1						
0.80.....	41.0	78	1.4	42.1	57.6	0.03
	51.0	61	2.0	33.2	66.8	.05
	67.0	35	1.4	40.8	58.6	.60
52 Ni-25 Co-19 Cr-4 C ANODE						
0.80.....	35.0	84	1.0	49.1	50.9	<0.1
	25.0	NA	3.8	11.8	44.3	7.9
	44.0	NA	3.2	15.4	49.0	7.1
52 Ni-25 Co-19 Cr-4 C ANODE, ELECTROLYTE pH = 1						
0.80.....	24.0	70	1.0	50.8	49.2	<0.01
	41.0	79	1.8	35.4	64.6	.04
	41.0	75	2.2	31.5	68.3	.12

NA Not available. Nap Not applicable.

NOTE.--Experiments were run for three sequential 8-h periods in each electrolyte (except 6 h for the final period for the ternary anode, pH 1), with a new cathode for each period.

In an effort to render insoluble a part of the chromium in the ternary Ni-Co-Cr anode in subsequent electrolysis, a heat was made in which carbon was added (as coke breeze) to a melt of the 55 Ni-25 Co-20 Cr alloy to partially carburize the chromium. It was postulated that the overall chromium solubility would be decreased because the chromium carbide would form insoluble anode sludge. The resultant alloy analyzed 3.9 pct C. A

24-h electrorefining test on an anode of this alloy, with the pH controlled at 1.0 ± 0.1 (table 3), indicated that about two-thirds of the chromium remained insoluble in the anode sludge. The maximum chromium in the final 8-h deposit was 0.12 pct; the spent electrolyte contained 3.5 g/L Cr. In the controlled-pH tests, the cathode CE remained higher with carbon-bearing anode material than with the carbon-free Ni-Co-Cr anode. This is

attributed, at least in part, to the lesser chromium concentration in the electrolyte.

An anode sludge was formed on the outside of the carbon-containing anode; the sludge analyzed 50 pct Cr, 15 pct C, and 15 pct each of Co and Ni. X-ray diffraction analysis verified that chromium carbide was a major phase in the anode sludge. The Ni-Co composition of deposits electrolyzed from the Ni-Co-Cr or Ni-Co-Cr-C anode at a pH of 1.0 were not greatly different. The Ni:Co ratio in the deposit from the carbon-bearing anode increased from about 1.0 after the first 8-h deposition to about 2.2 after the third sequential 8-h deposit.

Comparison of the 24-h controlled-potential electrolytic tests with the shorter term tests (8-h or less) conducted at the same cathode potential of -0.90 V and in the same intermediate-chloride electrolyte revealed that the cathode CE improved for longer deposition periods when using binary anodes. Good deposits were produced although the pH of the electrolyte changed from 1.0 at the start of the test to 5 at the end of the 24-h deposition period. Similar tests made on ternary anodes, without control of the pH to relatively low values, showed that a good deposit was obtained only during the first 8 h. After 8 h, the chromium level was apparently high enough to precipitate $\text{Cr}(\text{OH})_3$, as

the pH of the electrolyte had risen to 2.9. With pH control at about 1, deposits from the Ni-Co-Cr anode remained metallic for the 24-h period. The cathode CD values were higher with the binary anode than with the ternary anode.

CHROMIUM ADDITIONS TO ELECTROLYTE

Experiments were conducted to determine what effects Cr^{6+} and Cr^{3+} in the electrolytes have on the codeposition of Ni-Co alloy. These tests were run for 6 h, with the pH of the electrolyte maintained within a range of 1.0 to 1.3. A single binary anode, 70 Ni-30 Co, was used with a titanium cathode that had the back and sides masked off with tape. The intermediate-chloride electrolyte containing 6.5 g/L Co, 45 g/L Ni, 42 g/L Cl, and 34 g/L SO_4 was used, and 1 to 5 g/L Cr^{6+} or 1 to 8 g/L Cr^{3+} was added (doped) in the form of CrO_3 or $\text{Cr}_2(\text{SO}_4)_3$, respectively. The cathode potential was controlled at -0.90 V. The electrolytes were analyzed for Cr^{6+} (oxidation-reduction method) and total chromium before and after each test, and the deposits were analyzed for chromium, cobalt, and nickel. In the electrolytes, Cr^{3+} was determined by difference, i.e., total Cr - Cr^{6+} = Cr^{3+} . The cell voltage (between anode and cathode) was lower with the Cr^{6+} additions than with the Cr^{3+} additions (0.8 to 1.4 V versus 1.6 to 2.3 V). Data for these experiments are given in table 4.

TABLE 4. - Controlled-potential electrolytic experiments with chromium additions

Electrolyte		Cathode data		Chemical analysis					
Cr addition, g/L	pH	CD, A/ft ²	CE, pct	Spent electrolyte, g/L			Deposit, wt pct		
				Cr ⁶⁺	Cr ³⁺	Total Cr	Cr	Co	Ni
Cr ⁶⁺ :									
1.....	1.3	65	73	0	0.9	0.9	0.08	47.3	52.5
2.5.....	1.2	¹ 21	¹ 7	.7	1.6	2.3	4.8	25.9	54.5
5.....	1.1	17	1	4.7	.2	4.9	(²)	(²)	(²)
Cr ³⁺ :									
1.....	1.1	89	87	0	1.2	1.2	.05	49.9	49.7
4.....	1.2	54	73	0	4.1	4.1	.03	46.4	53.5
8.....	1.2	56	62	0	9.1	9.1	.25	49.4	49.7

¹Nonmetallic deposit. ²Not analyzed.

The test in which 1 g/L Cr^{6+} was added to the electrolyte had a cathode CE of 73 pct at a CD of 65 A/ft². The deposit analyzed 0.08 pct Cr, and the spent electrolyte analyzed 0.90 g/L Cr^{3+} , with no Cr^{6+} detected. Adding 5 g/L Cr^{6+} to the electrolyte lowered the cathode CE to 1 pct and the CD to 17 A/ft². The total deposit consisted of only about 0.03 g, not enough for analysis. The spent electrolyte analyzed 4.7 g/L Cr^{6+} and 4.9 g/L total Cr, indicating that about 0.2 g/L Cr^{3+} was in the spent electrolyte. An additional test, in which 2.5 g/L Cr^{6+} was added to the electrolyte, produced a nonmetallic deposit of 0.3 g. This test had a cathode CE of 7 pct and CD of 21 A/ft². The spent electrolyte analyzed 0.7 g/L Cr^{6+} and 2.3 g/L total Cr, indicating that the spent electrolyte contained 1.6 g/L Cr^{3+} .

The CD of electrolytes with Cr^{3+} additions decreased from 89 A/ft² for the 1-g/L addition to 54 A/ft² for 4 g/L. In the 1-g/L- Cr^{3+} electrolyte test, the cathode CE was 87 pct, but it dropped to 62 pct for the electrolyte containing 8 g/L Cr^{3+} . No Cr^{6+} was detected in either the initial or spent electrolytes when Cr^{3+} was added. The deposits from the 1-, 4-, and 8-g/L- Cr^{3+} electrolytes contained 0.05, 0.03, and 0.25 pct Cr, respectively, and roughly equal amounts of nickel and cobalt.

These experimental results indicate that Cr^{6+} has a much greater effect on Ni-Co deposition than does Cr^{3+} . At an electrolyte pH of 1.2, only ~1 g/L of Cr^{6+} can be tolerated without causing a drastic decrease in cathode CE and CD. Conversely, as much as about 9 g/L Cr^{3+} can be tolerated without greatly decreasing the CE, although some decrease occurs. The pH of chromium-containing electrolytes must be maintained at close to 1.0 in order to avoid cathodic formation of a compound presumed to be $\text{Cr}(\text{OH})_3$.

EFFECTS OF pH AND STIRRING RATE

A few short-term, 8-h tests were conducted at an initial pH of 2.0 for

the low-chloride electrolyte. For these tests, the cathode potential was controlled at -0.90 V without any additions to maintain the pH. Identical tests were performed on binary and ternary anodes. In both cases, the pH of the electrolyte had increased at the end of 8 h to the range of 2.5 to 3.0. The cathode CE was 96 pct for the binary and 88 pct for the ternary anode, and the anode CE was slightly lower for the ternary anode (96 pct versus 100 pct). The CD for the ternary anode was about half that for the binary anode. The Ni:Co ratio of the deposit was 1.0 for the binary anode test and about 0.9 for the ternary anode test. The latter anode resulted in 0.14 pct Cr in the cathode deposit.

Two 24-h tests were made on the ternary anode--with and without the pH controlled at 1.0. Without pH control, the deposit started to become nonmetallic after 8 h when the electrolyte contained about 2 g/L Cr. Conversely, metallic deposits were produced after 24 h when the pH was controlled at 1.0, although the electrolyte contained >9 g/L Cr. However, for this test, the cathode CE decreased as the chromium built up in the electrolyte, and the cathode CD increased with time. Without pH control, the CD decreased as chromium built up in the electrolyte.

Stirring rate experiments were conducted on binary 70 Ni-30 Co anodes using the intermediate-chloride electrolyte with the pH controlled at 1.0±0.2. Three stirring rates were evaluated--zero, medium, and fast (~900 rpm)--using a magnetic stirrer bar coated with Teflon fluorocarbon polymer. As the stirring increased, the Ni:Co in the deposit decreased from 2:1 (no stirring) to 1:1 (fast stirring), and the CE increased from 85 to 92 pct. The effect of stirring on Ni:Co in the deposit reflects a mass transfer polarization; stirring tends to replace depleted cobalt ions at the cathode electrolyte interface. As cobalt normally deposits more readily than nickel, disproportionate to the relative amounts of cobalt and nickel in the electrolyte, little or no stirring will tend to substantially increase the Ni:Co

ratio of the deposit. I.e., for the alloys under investigation, which contain substantially more nickel than cobalt, little or no electrolyte stirring will tend to balance the Ni:Co in the deposit to more nearly the Ni:Co ratio of the anode alloy.

EFFECTS OF HIGH CURRENT DENSITY

Results of electrolytic testing at a CD of 200 A/ft² indicated that the deposition rate for cobalt was decreased relative to the rate at low CD, with a

corresponding increase in the deposition rate for nickel. The use of high CD during the controlled-potential electro-deposition of Ni-Co alloy, in addition to a relatively slow stirring rate, will therefore help balance the Ni:Co ratio of the deposit to nearer the Ni:Co ratio of the soluble anode, from which the nickel and cobalt have been shown to dissolve in the proportions present. Anodic dissolution experiments verified that approximately uniform dissolution occurs with these anodes in acid sulfate-chloride electrolytes.

SUMMARY AND CONCLUSIONS

Detailed electrolytic experiments have been conducted using a controlled cathode potential mode, to assess effects of parameters such as Ni-Co-bearing soluble anode composition, SO₄:Cl electrolyte ratio, pH of the electrolyte, cathode potential, cathode CD, stirring rate, and chromium concentration on the deposition potential, cathode CE, Ni-Co alloy deposit composition, and extent of chromium codeposition in the Ni-Co alloy deposit.

The significant findings and conclusions of the controlled-potential electrolytic experiments (55° C) are summarized in the following discussion.

In experiments using both binary (70 Ni-30 Co) and ternary (55 Ni-25 Co-20 Cr) alloy anodes, the cathode CE increased as the SO₄:Cl ratio was decreased (chloride increased) from 5.10 to 0.04 and as the cathode potential was controlled at more negative values. For the Ni-Co-Cr anode, the high-chloride electrolyte produced the highest CE values throughout the range of cathode potentials.

The cathode CD was highly dependent upon the cathode potential, for both the Ni-Co and Ni-Co-Cr anodes. For both, the CD increased markedly as the potential was moved to more negative values between -0.65 and -1.10 V. For a given potential for both anodes, the lowest CD values generally occurred for the low-chloride electrolyte. For the binary anode, the highest CD values

resulted with the intermediate-chloride electrolyte; for the ternary anode, the highest CD values occurred for the high-chloride electrolyte.

When both the Ni-Co and Ni-Co-Cr anodes were used, the cathode CE dropped off rapidly at cathode CD values below about 13 to 20 A/ft². The CE tended to reach a relatively constant level for cathode CD values above about 20 A/ft². For both anodes, the CE was substantially lower for the low-chloride electrolyte than for the intermediate- and high-chloride electrolytes. For the binary anode, the CE plateau values were approximately the same for high-chloride and intermediate-chloride electrolytes. For the ternary anode, the highest cathode CE values occurred for the high-chloride electrolyte.

In experiments with both the Ni-Co and Ni-Co-Cr anodes, the higher percentages of cobalt and lower percentages of nickel codeposited in the Ni-Co alloy at potentials of -0.75 and -0.90 V. For both the binary and ternary anodes, the maximum cobalt and minimum nickel codeposited when the low-chloride electrolyte was used.

For both anodes, decreased cobalt and increased nickel were obtained in Ni-Co alloy deposits with increased cathode CD above about 15 A/ft². For a given CD, the cobalt was highest and the nickel lowest for the low-chloride electrolyte.

For both anodes, the lower Ni:Co ratios in the deposits occurred for the intermediate potential values of -0.75 and -0.90 V. The higher ratios occurred for the potential of -1.10 V, when the intermediate-chloride electrolyte was used with the binary anode and when the intermediate- and high-chloride electrolytes were used with the ternary alloy anode.

A potential of -1.10 V with the high- and intermediate-chloride electrolytes produced Ni:Co deposit ratios closest to the Ni:Co ratio of the binary anode. The latter electrolyte resulted in the highest cathode CE and cathode CD. For the ternary anode, the same behavior occurred, except that the highest cathode CE and cathode CD occurred for the high-chloride electrolyte.

Both a decreased stirring rate of the electrolyte and a high cathode CD increased the Ni:Co ratio of the deposits.

Brief tests in an all-sulfate electrolyte indicated that the potential for Ni-Co alloy deposition shifts somewhat in a more negative direction in comparison with the deposition potential when using relatively high-chloride electrolytes. Anode dissolution was restricted when using the Ni-Co-Cr anode for the all-sulfate electrolyte. For the intermediate- and high-chloride electrolytes, anode dissolution rates consistently exceeded deposition rates.

Hexavalent chromium (Cr^{6+}) has a detrimental effect on Ni-Co deposit efficiency. At an electrolyte pH of 1.2, the maximum Cr^{6+} that can be tolerated is ~1 g/L. When this limit was exceeded, a drastic decrease in both cathode CE and CD occurred. However, Cr^{6+} was not identified in anodically dissolved chromium-bearing alloy, only trivalent chromium (Cr^{3+}).

Appreciable amounts of Cr^{3+} can be tolerated in an acid sulfate-chloride electrolyte without chromium codepositing

with Ni-Co to any extent, as long as the pH is maintained at <1.5. However, increased amounts of Cr^{3+} in the electrolyte caused the cathode CE to decrease. If the pH gets as high as about 2.0, a nonmetallic coating, probably $\text{Cr}(\text{OH})_3$, forms on the cathode.

Encouraging results were obtained from Ni-Co-Cr anodes that had been melted with carbon additions. Solubility tests on these anodes indicated that only about one-third of the chromium in the anode was soluble, and the remainder of the chromium was accounted for as insoluble chromium carbide in the anode sludge.

Basic information derived from the electrolytic experiments on Ni-Co and Ni-Co-Cr anodes has been used to select operating parameters for controlled-potential deposition of Ni-Co alloys from more complex multicomponent superalloy scrap anodes, for which experiments are now in progress.

Acid chloride-sulfate electrolytes ranging from roughly equal concentrations of chloride and sulfate to substantially higher concentrations of chloride are needed for adequate dissolution of Ni-Co-Cr-bearing anodes and controlled-potential deposition of Ni-Co alloys. The results are best when the chloride substantially exceeds the sulfate content.

For electrolytes of adequate chloride content, controlled potential values in the more negative end of the -0.60 to -1.10 V versus SCE are required to obtain the better values of cathode CD, cathode CE, and Ni-Co alloy deposition rates.

The more negative cathode potentials have the added advantage of increasing the nickel content of Ni-Co alloy deposits relative to cobalt, tending to produce Ni:Co deposit ratios more consistent with the ratio of the anodes. This has importance for longer term depositions, to minimize electrolyte buildup of nickel

or cobalt. Minimal stirring of the electrolyte also favors this behavior.

For chromium-bearing anodes, the pH of the electrolyte must be controlled at <1.5 to sustain Ni-Co deposition without the tendency for nonmetallic chromium deposition (probably as the hydroxide) to occur, with a concomitant decrease in cathode CE. With pH control, appreciable amounts of Cr^{3+} , the species resulting

from anode dissolution, can be tolerated in the electrolyte without substantial reduction of cathode CE.

Melt carburization in anode preparation has the benefit of tying up as carbide a major part of the chromium and probably other elements such as tungsten and molybdenum, which, rather than solubilizing in the electrolyte, remain as an anode sludge.

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