PULSE PLATING OF NICKEL DEPOSITS

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BDX-613-2378
Distribution Category
UC-[redacted]25

Manuscript Submitted
67th Annual AES Technical Conference
American Electroplaters Society
June 22-26, 1980
Milwaukee, Wisconsin

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A prime contractor with the United States Department of Energy under Contract Number DE-AC04-76-DP00613

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PULSE PLATING OF NICKEL DEPOSITS

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ABSTRACT

Pulse plated and conventional nickel deposits have been compared for differences in morphology, mechanical properties, and microstructure. The deposits were obtained from nickel sulfamate, nickel chloride, and Watts nickel plating solutions. No significant differences were found in the direct and pulse current deposits from the sulfamate and chloride solutions; however, significant differences in microstructure, yield strength, and microhardness were observed in deposits from the Watts nickel solution.

Introduction

In the electroplating industry, the choice of an electrodeposit, such as nickel, in a particular application is based on its properties. The main properties that determine the value of a nickel coating applied for decorative purposes are color, reflectivity, hardness, and abrasion resistance. Porosity and certain chemical properties determine corrosion resistance. In the case of heavy nickel deposits for electroforming purposes, different properties are important. Here, the important properties are mechanical, such as internal stress, tensile strength, hardness, ductility, and yield strength. These properties of nickel electrodeposits can be varied over a wide range by changing deposition conditions, by changing the bath formulation, or by introducing chemical additives. Pulsed plating is a new technique used to alter properties of electrodeposits. Avila and Brown[1] found pulse plating eliminated the need for additives to improve nickel deposits from a Watts solution and that the deposit brightness extended over a greater current density range than the additives. In addition, pulse plating inhibits columnar growth and produces a fine grained structure. Raub and Viswanathan[2] found that the nickel structure loses its columnar configuration at low duty cycles and high frequency values. Popov, et al,[3] found that pulse plating of nickel gave smoother, less porous deposits. Leaman and Kownacki[4] found that pulse plating of the nickel diffusion barrier prior to gold plating

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*Operated for the U.S. Department of Energy by The Bendix Corporation, Kansas City Division under Contract No. DE-AC04-76-DP00613.

resulted in a 40 percent decrease in the porosity of the gold deposit.

Pulse plated and conventional nickel deposits were compared for differences in morphology, mechanical properties, and microstructure. Scanning electron microscopy (SEM) was used in the morphology studies; X-ray pole figure analyses and transmission electron microscopy (TEM) were used in the microstructural investigation. The mechanical properties determined were tensile strength and elongation by tension testing and microhardness.

Experimental

The nickel deposits characterized were obtained from nickel sulfamate, nickel chloride, and Watts nickel plating solutions. The composition and operating conditions of these plating solutions are given in Table 1.

The plating cell was a cylindrical glass container which accomodated 2 L of plating solution; the cathode-to-anode spacing was 1 inch (25 mm). Agitation was by means of a magnetic stirrer. Temperature of the plating solutions was kept within ±2°C of the operating temperature, and the pH was controlled to ±0.2 units. The pulse plating power supply was a square wave unit.

Some definitions of terms used in pulse plating are in order. The average current density ($\bar{i}$) is defined as:

$$\bar{i} = i_p \frac{t_{on}}{t_{on} + t_{off}} \qquad (1)$$

where

i_p = peak current density (A/dm^2),

t_{on} = on time (ms), and

t_{off} = off time (ms).

Average current densities are used in this paper. The duty cycle (D), or the percentage of the time the current is on, is defined as

$$D = \frac{t_{on}}{t_{on} + t_{off}} (100) \qquad (2)$$

Results have been reported on duty cycles with an on time of 1 ms and the off time adjusted to obtain duty cycles of 20, 33, and 50 percent.

Table 1. Composition and Operating Conditions of Nickel Plating Solutions

	Watts	Chloride	Sulfamate
Nickel Sulfamate (g/L)			250
Nickel Sulfate (g/L)	330		
Nickel Chloride (g/L)	45	300	
Boric Acid (g/L)	40	40	40
Magnesium Chloride (g/L)			3.5
pH	2.5	2.5	3.8
Temperature (°C)	55	55	60

Concentration of the wetting agent is the same in all the plating solutions.

For the SEM samples, highly polished brass substrates were inserted in a plastic holder with a gasket so the edges and back of the substrate were masked, leaving an area of 0.085 ft^2($8.7 \times 10^{-5} m^2$) to be plated. Prior to pulse plating, the substrates were cleaned with a mild alkaline cleaner, treated with a 10 volume percent sulfuric acid solution, and water rinsed after each step. Nickel deposits were obtained from the three plating solutions at current densities of 2 to 12 A/dm^2, and the cathode efficiencies were determined from the weight of the deposit and the ampere-minutes recorded by the integrator of the pulse plating power supply. Thicknesses of these nickel deposits were approximately 2 μm.

Nickel deposits used for the measurement of the mechanical and microstructural properties were plated on 6061 aluminum substrates with one side masked. Prior to nickel plating, the substrates went through a cleaning process, double zincating, and copper deposition from a copper strike solution. Nickel was plated at a current density of 4 A/dm^2 to thicknesses in the 100 to 150 μm range. After removing the maskant, the aluminum was dissolved in a hydrochloric acid solution and the copper in an ammonium persulfate solution. These nickel foils were chemically analyzed using emission spectroscopy and metallurgically cross-sectioned for microhardness and thickness determinations. The cross-sections also were used for grain structure examinations. Tensile strength and elongation of these nickel foils were determined by tension testing using ASTM E345-69. The subsize specimen was used, and the foils were interleaved with hard aluminum sheet during machining. This nickel foil was also used in the microstructural studies.

Results and Discussion

Pulsed and conventional nickel deposits from nickel sulfamate, nickel chloride, and Watts nickel plating solutions were analyzed chemically. The purity of the deposits ranged from 99.22 to 99.82 weight percent; the major contaminant was cobalt, with concentrations from 0.1 to 0.7 weight percent. Cobalt is introduced into these solutions from the nickel salts and nickel anodes. Other contaminants found were copper, iron, silicon, magnesium, and calcium at concentrations of 0.08 weight percent or less. No trends were obvious concerning the influence of pulse plating on the impurity levels in the nickel deposits.

Cathode efficiencies for the pulsed and direct current processes were determined over the current density range of 2 to 12 A/dm^2 for the three nickel plating solutions and are shown in Figure 1. Some trends common to all the plating solutions were observed. In general, the cathode efficiencies using direct current are greater than those using pulsed current. Up to about 4 A/dm^2, the cathode efficiencies for pulsed current processes are about the same (92 to 94 percent), regardless of the duty cycle. With increasing current density and lower duty cycles, the cathode efficiency steadily drops and falls as low as 80 to 85 percent in some cases. With a 50 percent duty cycle, the cathode efficiency parallels the direct current processes and differ by 2 to 8 percent. The greatest difference is at low current densities and the least at high current densities.

Exceptions to these trends are found in the Watts nickel plating solution. Instead of the cathode efficiency gradually decreasing with the current density for the direct current process, a maximum occurs at 5 to 6 A/dm^2. At low current densities with a 50 percent duty cycle, the cathode efficiency exceeds that for direct current plating.

Surface Morphology

The surface morphology of the nickel deposits from the sulfamate, chloride, and Watts nickel plating solutions was investigated using the SEM. In Figure 2, SEM photomicrographs of direct and pulsed current nickel deposits from a sulfamate solution are shown. These rounded and granular appearing deposits are representative of the nickel deposits obtained from various combinations of current density and duty cycle. Finer surface features were not obtained with pulsed current. In Figure 3, SEM photomicrographs of direct and pulsed current deposits from a nickel chloride solution are shown. These deposits have surface features that are pointed and faceted, as opposed to rounded. In general, the pulsed current deposits have finer surface features than the direct current deposit.

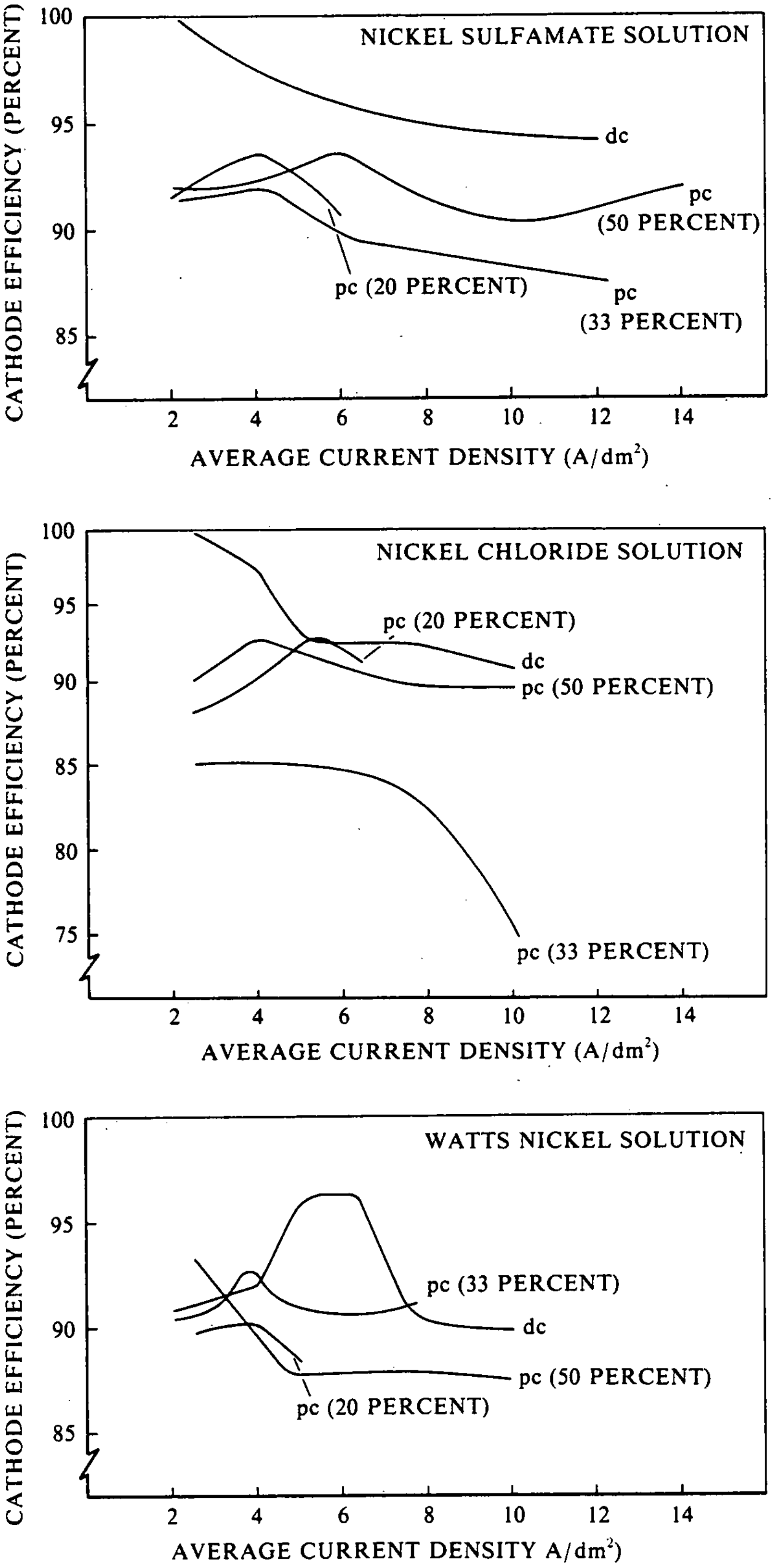
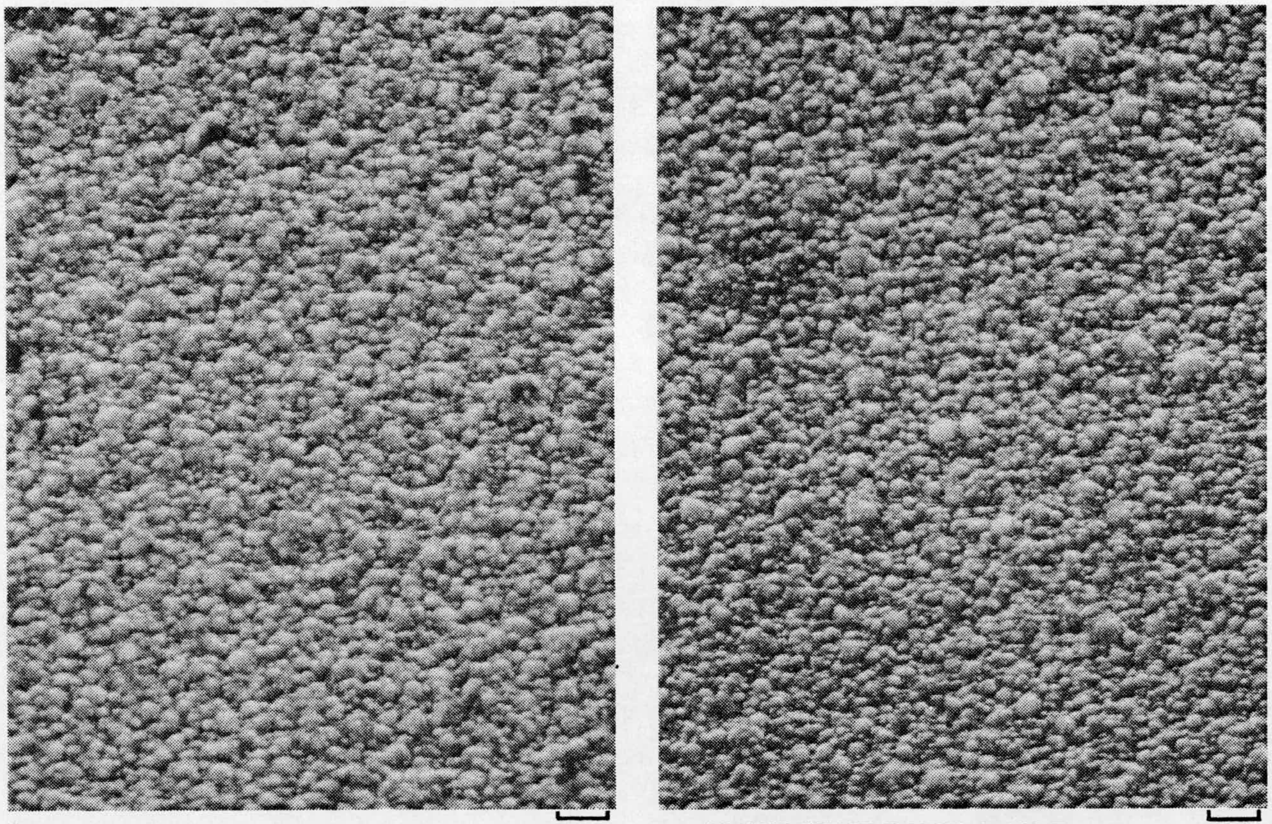


Figure 1. Cathode Efficiencies



dc — 4 μm

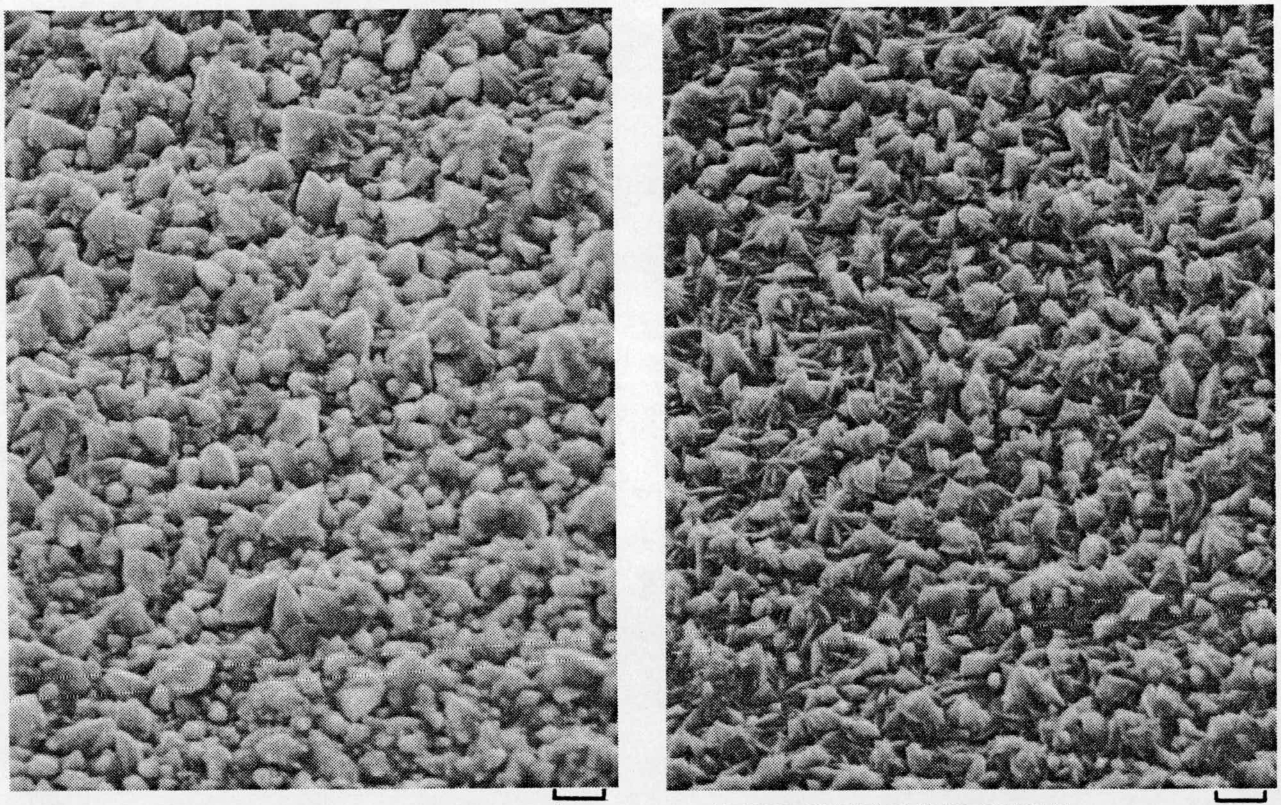
pc, 33 PERCENT DUTY CYCLE — 4 μm

Figure 2. Nickel Deposits From a Sulfamate Electrolyte, 4 A/dm^2

The most prominent changes in surface morphology with pulse plating occurred with the Watts nickel plating solution. In Figure 4, SEM photomicrographs of direct and pulsed current deposits from a Watts nickel solution are shown. The direct current deposit has large granular features and distinct grain boundaries. With a 50 percent duty cycle, the granular features appear to be finer and create a more compact deposit between the fewer observed large granular features. At a 33 percent duty cycle, the granular features of the pulsed nickel deposit are finer and a more homogeneous surface appearance results. With a 20 percent duty cycle, the coarser granular features reappear, but not to the extent of the direct current deposit. The current density of 4 A/dm^2 was used in obtaining these nickel deposits.

Mechanical Properties

The mechanical properties of the pulsed and direct current nickel deposits from the three nickel plating solutions were determined at a current density of 4 A/dm^2. The yield strength and elongation were an average of four determinations. Results were rejected if the sample fractured outside the gage length. The microhardness results were an average of five measurements.



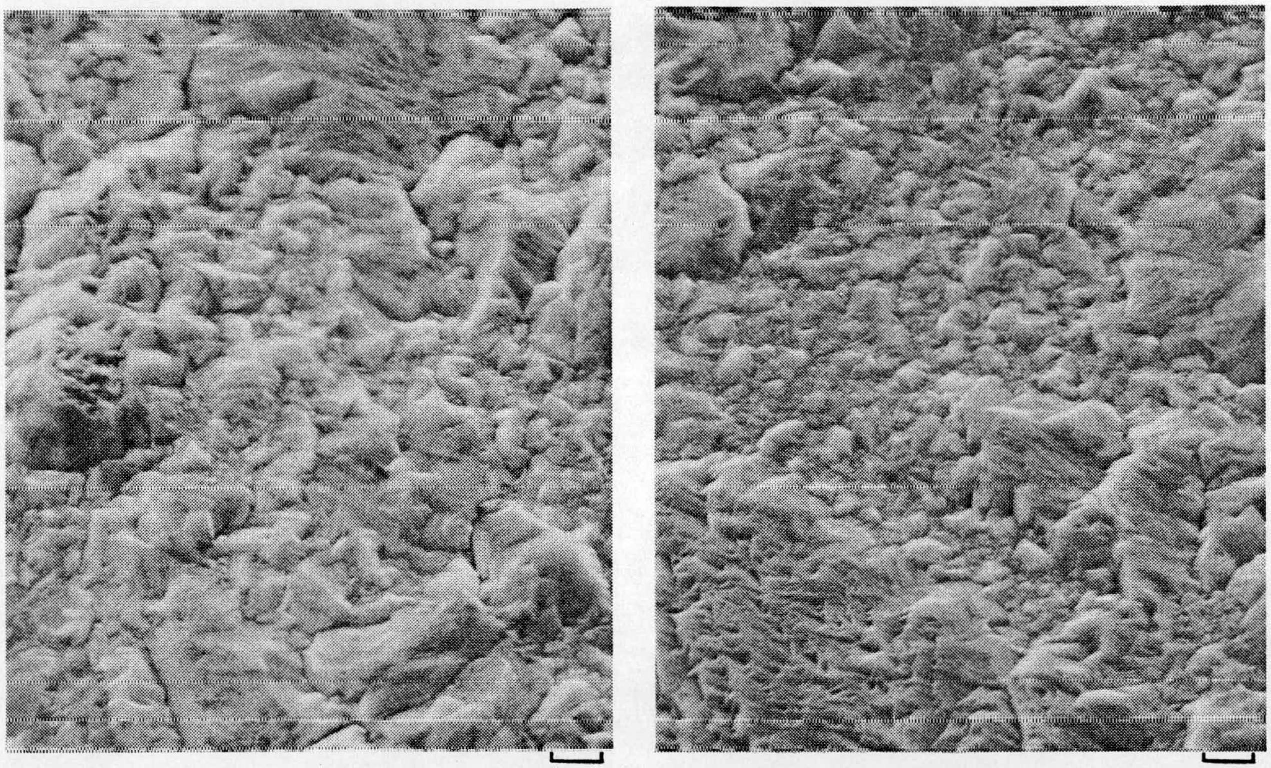
dc

pc, 33 PERCENT DUTY CYCLE

Figure 3. Nickel Deposits From a Chloride Electrolyte, 4 A/dm^2

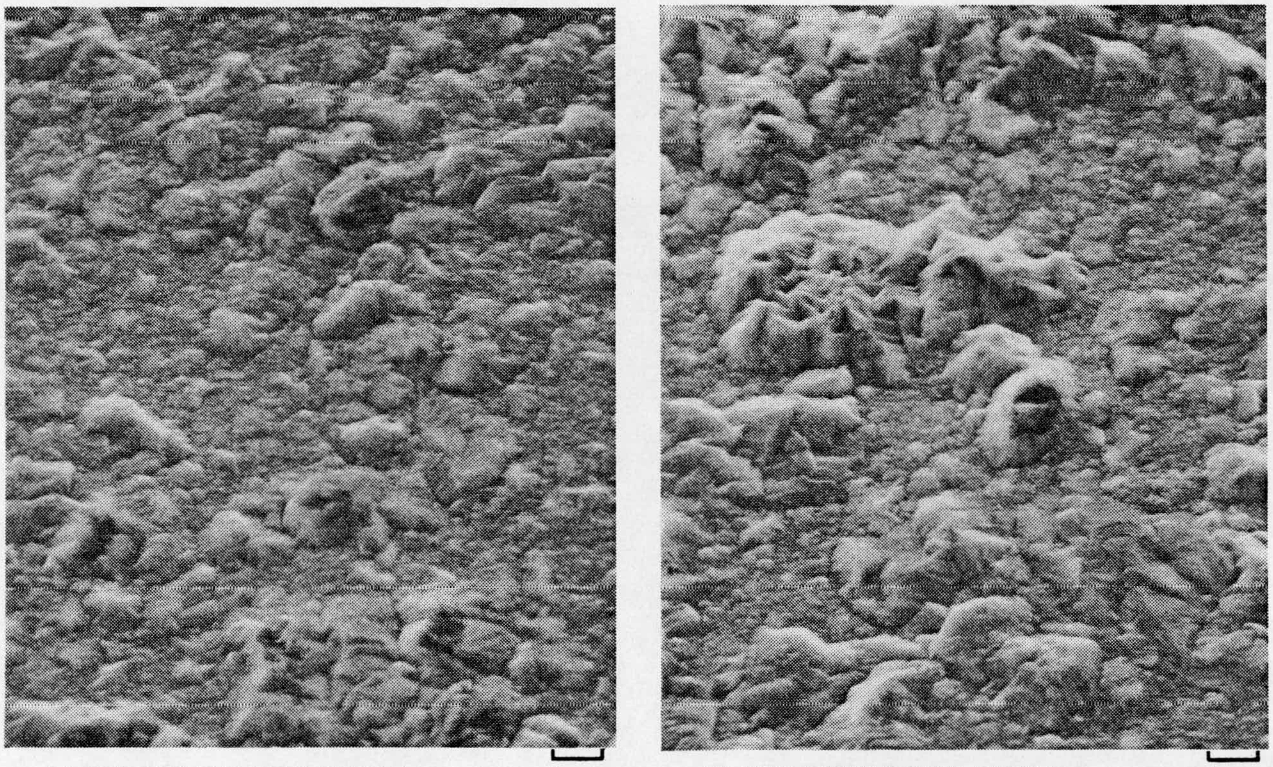
The mechanical properties of nickel deposits from a nickel sulfamate plating solution are given in Table 2. The yield strengths of the pulse plated deposits for the 20 and 33 percent duty cycles are about 15 percent higher than direct current deposit. The microhardness and elongation for the pulse plated and direct plated nickel deposits are similar. Comparing the yield strength and elongation of these nickel deposits to literature values[5] reveals some discrepancies. Although the yield strengths are in agreement, the elongation test results are significantly lower. The scatter of the results was relatively high for the elongation measurements and could be caused either by intrinsic defects in the nickel deposits or by defects at the machined edges of the samples. The measured values ranged from 1 to 7 percent for the elongation in these samples. The microhardness results are somewhat higher than those reported elsewhere.[6]

Mechanical properties of nickel deposits from a nickel chloride plating solution are shown in Table 3. No significant difference was found in yield strength, elongation, and microhardness of pulse and direct current nickel deposits. These yield strengths compare well with literature values.[5,7] However, as in the case



dc

pc, 50 PERCENT DUTY CYCLE



pc, 33 PERCENT DUTY CYCLE

pc, 20 PERCENT DUTY CYCLE

Figure 4. Nickel Deposits From a Watts Electrolyte, 4 A/dm^2

Table 2. Mechanical Properties of Nickel Deposits From a Sulfamate Electrolyte at 4 A/dm^2

	Yield Strength* (MPa)	Elongation** (Percent)	Microhardness***
dc	606	4.5	368
pc, 50 Percent Duty Cycle	562	5.0	343
pc, 33 Percent Duty Cycle	729	2.3	375
pc, 20 Percent Duty Cycle	703	4.8	380

*At 0.2 percent offset.
**1-inch (25.4 mm) gage.
***Knoop, 100-g load.

Table 3. Mechanical Properties of Nickel Deposits From a Chloride Electrolyte at 4 A/dm^2

	Yield Strength* (MPa)	Elongation** (Percent)	Microhardness***
dc	544	10.7	319
pc, 50 Percent Duty Cycle	589	9.8	326
pc, 33 Percent Duty Cycle	563	6.0	334
pc, 20 Percent Duty Cycle	560	8.3	329

*At 0.2 percent offset.
**1-inch (25.4 mm) gage.
***Knoop, 100-g load.

of the sulfamate nickel deposits, elongation was lower than expected, with a considerable scatter in the results (from 2 to 13 percent). Microhardness was comparable with those reported elsewhere.[7]

The most significant changes in mechanical properties of nickel deposits induced by pulsed plating was observed with a Watts nickel plating solution. These results are given in Table 4. The yield strengths of the pulse plated deposits are an average of 35 percent higher than the direct current deposits. Again, the elongation results were lower than expected,[7] and the high scatter of results prevented making comparisons between pulsed and direct current deposits. Typical scatter was 7 to 19 percent for the elongation of the 20 percent duty cycle deposit. Also, about a 25 percent increase in microhardness was noted for the pulse plated deposits. Yield strength and microhardness results of the conventional nickel deposits compared favorably with some literature values.[5,7]

Microstructure

Grain structures of the nickel deposits from the various plating solutions were obtained from metallurgical cross-sections. A fine grained, laminated structure was observed for nickel deposits from a sulfamate solution. Differences in pulsed and direct current deposits were not distinguished in this case or with the deposits from a nickel chloride solution. The deposits from a nickel chloride solution were fine grained. Changes in the grain structure were observed when comparing pulsed and direct current deposits from a Watts nickel solution. The direct current and pulsed current with a 50 percent duty cycle have a columnar structure with coarse grains. However, with a 20 and 33 percent duty cycle, the nickel deposits are obviously finer grained and appear to lose some columnar structure. Quantitative grain size determination was not possible because of the fine grain size.

With optical microscopy, significant microstructural differences occurred only between the direct and pulse plated Watts nickel deposits. As described previously, changes in surface morphology, yield strength, microhardness, and grain structure also were observed. Because of these changes, further microstructural studies were performed only with the nickel deposits from a Watts nickel solution.

X-ray Pole Figure Analysis

An X-ray pole figure plot is a contour map which graphically displays the scattering efficiency in various directions relative to some specific crystallographic plane. The plane generally is chosen to be the lowest index plane from which diffracted

Table 4. Mechanical Properties of Nickel Deposits From a Watts Electrolyte at 4 A/dm^2

	Yield Strength* (MPa)	Elongation** (Percent)	Microhardness***
dc	364	14.0	225
pc, 50 Percent Duty Cycle	563	5.0	259
pc, 33 Percent Duty Cycle	498	8.5	282
pc, 20 Percent Duty Cycle	436	12.7	290

*At 0.2 percent offset.
**1-inch (25.4 mm) gage.
***Knoop, 100-g load.

intensity is obtained. This plane is the (111) plane for face-centered cubic materials such as nickel. The scattering power is directly proportional to the probability that a grain in the bulk is properly oriented for diffraction. Specific orientations are identified by the use of a series of standard stereographic projections. The high intensity regions of the measured pole figure are matched with the location of the desired diffraction plane (the (111) plane in this case) on the projection. All four nickel foils show a cylindrical symmetry, implying no preferred orientation of the grains relative to a direction on the surface. A preferred orientation is shown in Table 5 for the nickel deposits obtained at 4 A/dm^2 from a Watts nickel solution. These deposits have a fiber texture and also possess dual textures. The primary texture is listed first in Table 5. The texture is a function of many plating variables, principally current density, the electrolyte, temperature of the electrolyte, agitation, and pH. The direct current nickel deposits, which have a principal (100) orientation, exhibit the highest ductility and lowest hardness (Table 4). This relationship of ductility and hardness to (100) oriented nickel deposits has been pointed out by Leidheiser[8] and Evans.[9] Pulse plated deposits with (211) and (111) orientations are inhibited modes of growth for nickel deposits. The appearance of (111) occurs only when all other modes of growth are severely inhibited. This inhibition has been reported[10] to stem from the abundant formation of $Ni(OH)_2$ near the cathode because of a localized pH increase. As the duty cycle is lowered and the pulse current density is increased, more

Table 5. Correlation of Duty Cycle and Preferred Orientation for Nickel Deposits From a Watts Solution at 4 A/dm^2

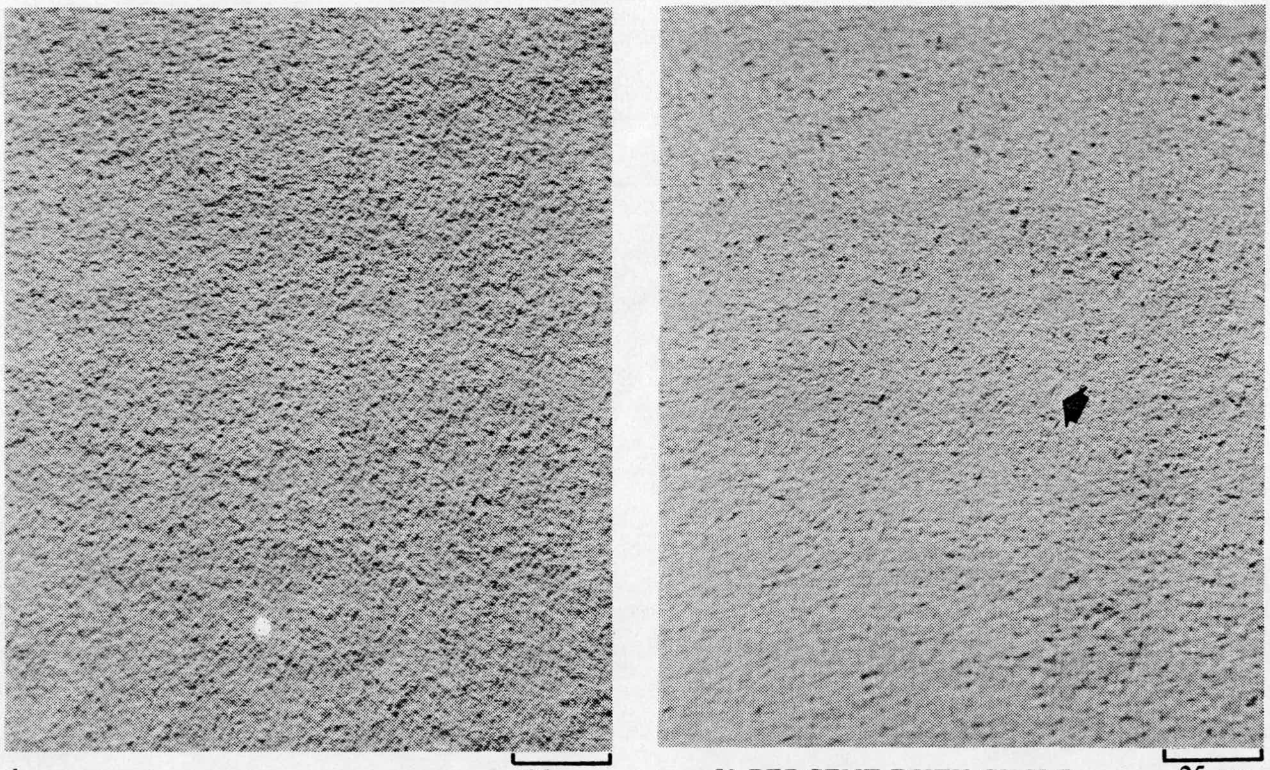
Duty Cycle (Percent)	Preferred Orientation
dc	(100) + (111)
50	(211) + (311)
33	(220) + (311)
20	(111) + (311)

hydrogen is formed at the cathode surface, favoring this type of inhibition. This same type of change in orientation of nickel deposits occurs when the organic additive, butynediol (but-2-yne 1,4 diol), is used in a Watts nickel solution. Amblard et al,[11] indicate orientation changing from (100) to (211) with the addition of butynediol. At the highest additive concentrations, the orientations further change from (211) to (111).

X-ray diffraction examination also indicates the bulk behavior of each nickel sample is different with respect to each other. The (111) reflection is the basis for comparison and is normally expected to be the most intense line, as is the case for the pulse plated nickel deposits. However, the direct current deposit shows the (200) reflection to be the most intense by far. All the pulse plated deposits show roughly similar overall intensities except the relative intensities of the (200) and (220) reflections. The (331) and (420) reflections are generally less than expected.

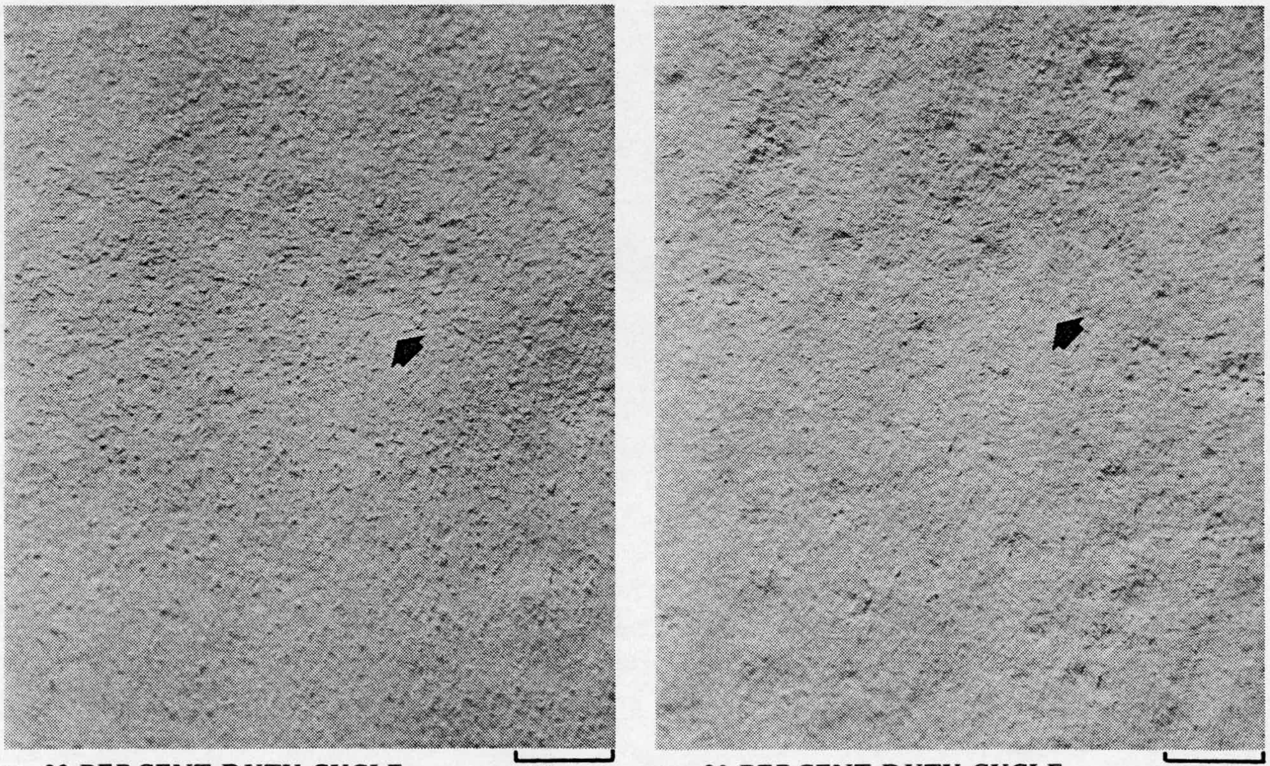
Optical and Electron Microscopy

Optical photomicrographs of the nickel deposits from a Watts nickel solution are shown in Figure 5. In all cases, the grain size appears to be very small. The amount of twinning apparently increases with pulse plating. (Arrows in these photomicrographs indicate twinning.) In the pulse plated nickel deposits, twinning increases as the duty cycle decreases. Twinning is an event that takes place with a defined probability during growth of crystallites and depends on the conditions of electrolysis. In general, nickel deposits from a Watts nickel solution have a small amount of twinning. Apparently, pulse plating greatly increases the probability of twinning.



dc

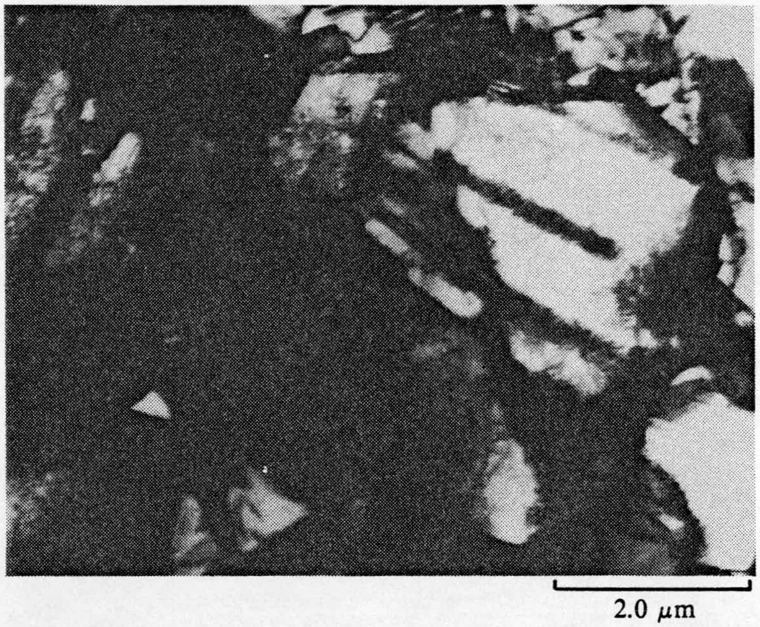
pc, 50 PERCENT DUTY CYCLE



pc, 33 PERCENT DUTY CYCLE

pc, 20 PERCENT DUTY CYCLE

Figure 5. Optical Photomicrographs of Nickel Deposits From a Watts Nickel Solution



dc

pc, 20 PERCENT DUTY CYCLE

Figure 6. Transmission Electron Photomicrographs of Nickel Deposits From a Watts Nickel Solution at 4 A/dm^2

Transmission electron microscopy also verifies the extremely fine grained nature of these nickel deposits as shown in Figure 6. The grain size is roughly the same for the direct current and all pulse plated deposits. Generally, the grains range from 0.4 to 2.5 μm in diameter. The dislocation density, the number of stacking faults, and twinning increase dramatically for pulsed plated nickel deposits obtained at 33 and 20 percent duty cycles. Again, twinning is by far the dominant feature in all cases and is indicated with an arrow in Figure 6.

Conclusions

In general, no significant differences in direct and pulse current nickel depostis from sulfamate and chloride solutions were found. However, differences were observed in nickel deposits from a Watts nickel solution. These pulse plated nickel deposits had grain sizes ranging from 0.4 to 2.5 μm, a 35 percent increase in yield strength, and a 25 percent increase in microhardness when compared to direct current deposits. Also, the surface morphology of these nickel deposits becomes less pyramidal in character when pulse plating is used. Generally, pulse plating greatly influences the preferred orientation of all the nickel deposits from this solution. Primary and secondary orientations are observed in all the deposits. In addition, pulse plating at low duty cycles dramatically increases the probability of twinning in these nickel deposits.

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