The Effect of Direct-reverse Pulse Parameters On the Morphology & Corrosion Resistance Of Nickel Deposits

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When electrodeposited nickel is used in the corrosion protection of steel, two factors are important: the porosity and corrosion resistance of the coating. The optimum direct-reverse pulse parameters of nickel deposits were determined using factorial experiments. Compared to direct current plating, electrodeposition of nickel using pulse plating can provide coatings with lower porosity and improved corrosion resistance. The reason for this is found in the distinct changes in texture and crystallite size as measured by XRD and SEM studies.

The effect of pulse plating on electrodeposited nickel has been described in several studies. Grain size refinement by the application of a relatively high-frequency (>10 Hz) pulse current has been reported by Paatsch[1] and others.[2,3] The effect of pulse current on the surface roughness and porosity has also been studied.[4] Fewer results have been reported on the reverse pulse plating of nickel.[5,6]

A correlation between the crystal orientation planes and the corrosion potential during anodic polarization has been reported.[7] Others have studied the growth of nickel crystals on different substrates as influenced by pulse plating conditions.[8] Here, we have concentrated on steel substrates and production-applicable frequencies and equipment. We have studied the effect of direct, pulse and pulse-reverse plating parameters on the porosity and corrosion resistance and found the optimum production parameters for nickel pulse plating. This data can be applied industrially. Further, we analyzed the relationship between the texture and the deposit properties.

Table 1
Factorial Experiment Results:
Effect of Variables on Deposit Porosity, pores/cm²

Condition No.	Frequency, Hz	Forward Duty Cycle	Reverse Duty Cycle	Porosity, pores/cm²
1	50	10%	0%	4.2
2	50	20%	5%	2.0
3	50	50%	10%	5.1
4	100	10%	5%	2.0
5	100	20%	10%	1.5
6	100	50%	0%	6.0
7	200	10%	10%	3.0
8	200	20%	0%	3.0
9	200	50%	5%	5.3
10	-------Direct Current---------			8.0

Table 2
Pulse and DC Plating Conditions Used in Corrosion, SEM & XRD Studies (avg. current density, 3 A/dm²)

Pattern	Frequency, Hz	Forward Duty Cycle	Reverse Duty Cycle	Pulse no. ratio
Periodic reverse	100	20	5	10
Periodic pulse	100	50	—	10
Direct current	—	—	—	—

Experimental Procedure

The experiments were carried out in a Watts nickel solution with the following composition and conditions:

Nickel sulfate, $NiSO_4 \cdot 7H_2O$	240 g/L
Nickel chloride, $NiCl_2 \cdot 6H_2O$	40 g/L
Boric acid, H_3BO_3	40 g/L
Sodium dodecyl sulfonate, $C_{12}H_{25}SO_3Na$	0.05 g/L
Benzoic sulfamide, $(C_6H_4 \cdot CHO_3NS)$	0.8 g/L
Butynediol / pyridine additives	0.2 g/L
Temperature	50ºC
Agitation	None

The average current density for pulse plating was held the same as that for direct current plating, *i.e.*, 3.0 A/dm². The direct current study was used as a basis for comparison.

All pulse plating was carried out using a computer-aided pulse plating system. It consisted of a rectifier and an interface to a computer capable of performing precise programming and execution of the pulse waveforms.

The porosity of the nickel deposits was measured by a filter paper method. Filter paper containing the test solution was overlaid on the surface of the sample. Deposit porosity, in pores/cm², was defined as the number of blue points showing per square centimeter of filter paper. The composition of the test solution was 10 g/L $KFe(CN)_4$ and 20 g/L NaCl.

Results & Discussion

After studying the effect of pulse parameters on the porosity, including forward and reverse pulse frequency, duty cycle and the ratio of the number of forward pulses to the number of reverse pulses, we selected three factors and levels for a factorial experiment.[9] The goal was to determine the optimum production parameters to minimize nickel porosity. The results are shown in Table 1.

Using the expected-mean-square rules,[9] we made several observations. The forward duty cycle was found to be the most significant factor in affecting nickel deposit porosity. The second most significant factor was pulse frequency. From our analysis, the optimum operating parameters were:

Frequency	100 Hz
Forward duty cycle	20%
Reverse duty cycle	5%
Pulse number ratio	10

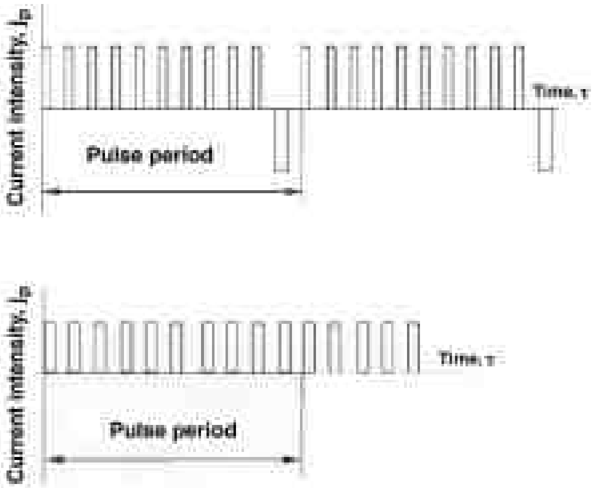

Fig. 1—Pulse current patterns (Average current density = 3 A/dm²): (a) periodic reverse pattern: cathode pulse current density = 20 A/dm², anode pulse current density = 20 A/dm², pulse period = 10 ms, forward pulse time = 0.2 ms and reverse pulse time = 0.5 ms; (b) pulse plated pattern: cathode pulse current density = 6 A/dm², pulse period = 10 ms and pulse time = 0.5 ms.

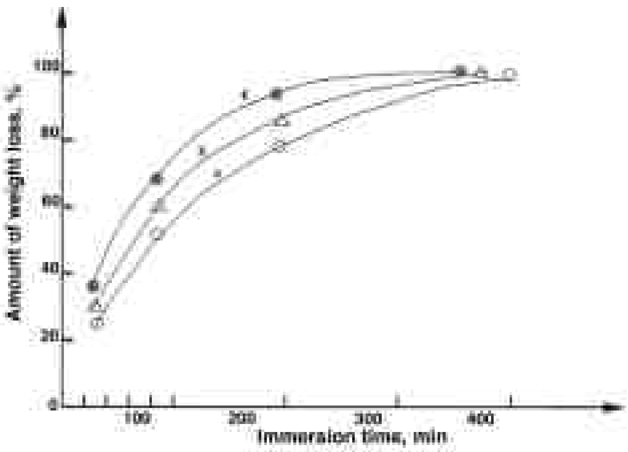

Fig. 2—Dissolution of nickel deposits in 7M HNO_3: (a) periodic reverse; (b) pulse plated; (c) direct current.

In order to compare the corrosion resistance and texture of the pulse deposits with those for the direct current deposits, we performed corrosion tests, scanning electron microscopy (SEM) and X-ray diffraction (XRD) experiments. The pulse and direct plating conditions used are listed in Table 2. The periodic reverse condition corresponded to the set of optimum parameters noted above. The periodic reverse and pulse plating conditions are shown in Fig. 1.

In the corrosion test, stainless steel was used as the substrate in order to avoid complications from the presence of dissolved substrate elements during the test. As shown in Fig. 2, the dissolution of plated nickel was measured in terms of weight loss (as a percent of initial deposit weight) as a function of time (min) in 7M HNO_3 solution. After 30 min in nitric acid, 25 percent of the periodic reverse deposits and 30 percent of the pulse plated deposits had been dissolved, while nearly 40 percent of the direct current deposits was dissolved. After 90 min, the nickel coating was completely stripped from a central circular area on both sides of the direct-current panel, while the panels with the two types of pulsed deposits remained free of perforations. Ultimately, after 360 min, all nickel on both panels had been dissolved. The morphology of the corroded surface after 60 min exposure was examined by SEM and is shown in Fig. 3. The surface of the pulse-reverse deposits plated under optimum conditions was the least corroded. The surface of the pulse-plated deposits corroded less severely than did the direct current deposits.

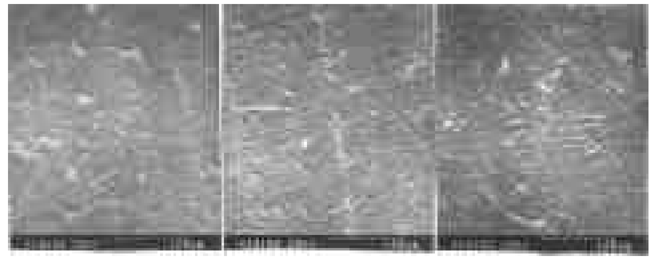

Fig. 3—Morphology of the corroded surfaces of the nickel deposits: (a) periodic reverse; (b) pulse plated; (c) direct current.

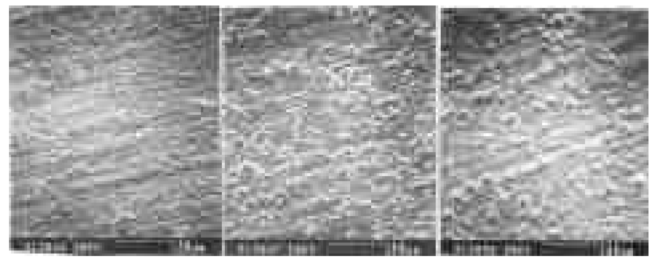

Fig. 4—Morphology of the nickel deposits: (a) periodic reverse; (b) pulse plated; (c) direct current.

The properties of the pulse deposits were superior to those of the direct current deposits, and are related to texture. Figure 4 shows SEM photos of the as-plated deposit morphologies. Compared to the direct current deposits, the grain size of the pulse-plated deposits was refined. As the forward duty cycle was decreased, the grain size was reduced. This observation is in agreement with the accepted theory of pulse plating.[3]

An analysis of the deposit texture is shown in Table 3 and Fig. 5, where the intensities are given as a percentage of the (111) line intensities. For comparison, the intensity ratios of the ASTM standard powder pattern are also shown in Table 3.[10]

For direct current and pulse plated deposits the (200) line was slightly dominant, while for the periodic reverse deposits the (200) line was strongly dominant, revealing

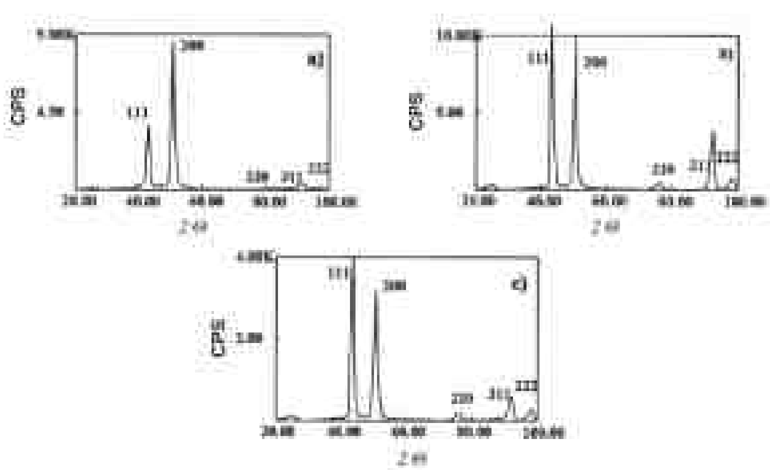

Fig. 5—X-ray diffraction patterns of the nickel deposits: (a) periodic reverse deposits; (b) pulse plated deposits; (c) direct current deposits.

significant texture versus the standard powder pattern.

Table 3
Texture in the Nickel Deposits by X-ray Diffraction

Reflection	Powder nickel	Periodic reverse	Pulse plated	Direct current
111	100	100	100	100
200	42	232	72	63
220	21	2	4	2
311	20	4	24	12
222	7	2	4	3

Conclusion

Electrodeposition of nickel using pulse-plating techniques can provide coatings with lower porosity and improved corrosion resistance as compared with direct current plating. The reason for this is found in the distinct changes in texture and the size of crystallites as determined by XRD and SEM studies, *i.e.*, refined grain size and preferred (200) crystal orientation of the pulse deposits.

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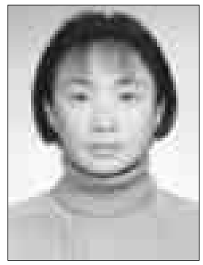

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