Nickel Coatings and Electroforming Using Pulse Reversal Plating

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Introducing pulse plating brings new life and possibilities to one the oldest groups of electroplating processes. Nickel coatings and electroforming are used in a great variety of products, from oil valves to optical discs, and for many applications such as corrosion protection and micro-mechanics.
A series of new results using pulse reversal plating in Watts based electrolytes will be discussed. Electroforming completely without internal stress and with improved throwing power will be demonstrated, as well as a corrosion resistance of nickel coatings that could allow coating thicknesses, as well as allergy risks, to be significantly reduced.

Introduction

Nickel plating is a relatively old process. The first nickel bath was formulated by C. P. Watts in 1916. This bath formulation is still used today, because it is relatively cheap and easy to operate and maintain.

The effect of pulse plating on electrodeposition of nickel, has been described in several studies. Grain size refinement as a result of pulsed current (PC) at relatively high frequencies (f > 20 Hz) has been reported by Paatsch [1] and others [2,3].

Fewer results have been reported on pulse reversal (PR) plating of nickel [3,4,5].

In this paper the following abbreviations will be used frequently:

DC Direct Current - Conventional plating at a constant current level.

PC Pulsed Current - Uni-polar waveform, e.g. a cathodic pulse followed by a pause (on/off plating) or cathodic pulses at alternating current levels.

PR Periodic current Reversal (or Pulse Reverse) - Bi-polar waveform, e.g. a cathodic pulse followed by an anodic pulse.

Other types of pulse patterns exist, using non square waveforms or combinations of the above, but we shall concentrate on the three basic forms.

The total time T for one cycle is either:

(for PC) $T = T_{on} + T_{off}$

or

(for PR) $T = T_c + T_a$

The frequency for PC and PR plating is $f = 1 / T$.

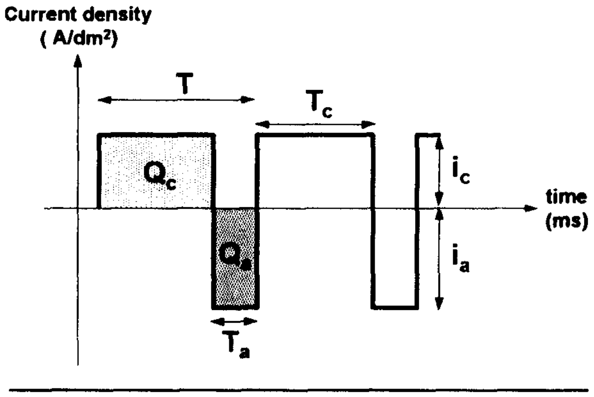

Figure 1: Typical PR pulse pattern.

In case of PR plating the total charge applied in one cycle is $Q = Q_c - Q_a$. The ratio Q_a / Q_c has a strong influence on several deposit properties, but since material is dissolved during the anodic pulse the total time could be increased significantly if this ratio gets too high.

Nickel bath composition

All the electrolytes used in this investigation are based on the Watts solution. Numerous versions of this bath exist, but the concentrations usually are: nickel sulphate 240-300 g/l, nickel chloride 40-60 g/l and boric acid 25-40 g/l [6].

The amount of nickel chloride in the bath strongly affects mechanical properties such as internal stress and hardness. A Watts bath with a high chloride concentration (more than 50 g/l) produces hard coatings with substantial (tensile) stress [6]. However, the chloride concentration also determines the solubility of the anodes, which are usually made of pure nickel for this type of bath. A low concentration of chloride makes it difficult to dissolve the anodes, except at very low current densities. This problem makes PR impossible, due to passivation of the surface during the anodic pulses.

For the corrosion protection part of this investigation, a typical Watts bath, referred to as W2, was compared to a bath (W3) in which some of the nickel sulphate had been substituted by nickel chloride. A third bath, with a very high concentration of chloride (W1) was used for electroforming. The composition of the three baths was as follows:

Nickel bath, W1 (pH=3.3):

50 g/l	Nickel sulphate, $NiSO_4 \cdot 6H_2O$
300 g/l	Nickel chloride, $NiCl_2 \cdot 6H_2O$
40 g/l	Boric acid, H_3BO_3

Nickel bath, W2 (pH=4.5):

300 g/l	Nickel sulphate, $NiSO_4 \cdot 6H_2O$
50 g/l	Nickel chloride, $NiCl_2 \cdot 6H_2O$
40 g/l	Boric acid, H_3BO_3

Nickel bath, W3 (pH=4.0):

250 g/l	Nickel sulphate, $NiSO_4 \cdot 6H_2O$
100 g/l	Nickel chloride, $NiCl_2 \cdot 6H_2O$
40 g/l	Boric acid, H_3BO_3

Electrochemical studies of two of these baths lead to several interesting results. Both of the two experiments illustrated in figure 1, were carried out at 50°C (122°F) using a rotating disc electrode (1000 rpm). After a suitable cathodic period at 2 A/dm^2, a potential sweep from approximately -600 mV (SHE) to 200 mV at 2 mV/s was conducted.

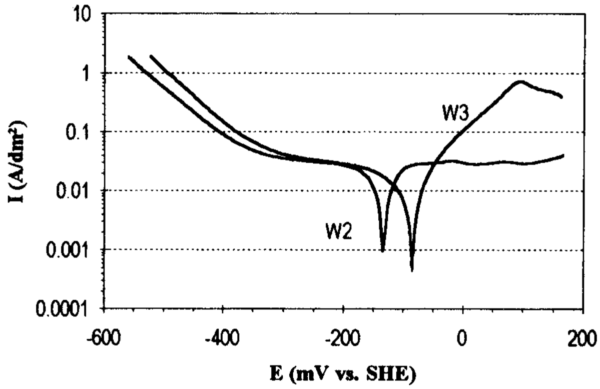

Figure 1: Potential sweeps showing the maximum anodic current density before passivation occurs in two of the three nickel baths used.

Studying the cathodic parts of the two curves, both baths appear to have a limiting current for the reduction of H^+ ions at approximately 0.02-0.03 A/dm^2. Moving further into the cathodic direction (from approximately -350 mV to -600 mV) this limiting current region is followed by a stable section which is expected to continue until the limiting current for the reduction of nickel ions is approached.

The anodic part of the curves (from approximately -100 mV to 200 mV) are the most interesting for this investigation, because of the significant difference in maximum anodic current density. The extra concentration of chloride (and smaller concentration of sulphate) in the W3 electrolyte clearly allows a faster dissolution of the deposited nickel (around 0.8 A/dm^2), which is just what is required for the desired effects of PR plating.

Nickel Coatings

This part of the investigation will concentrate on the improvement of nickel coatings for corrosion protection of mild steel. To protect a substrate against corrosive environments, two aspects are important. One is the grain size of the deposit which is directly responsible for the number of pores in the coating. Second is the corrosion rate of the nickel coating itself, since corrosion of the nickel will create pores that were not critical from the beginning.

Preparing samples

After the electrochemical investigation it was decided to use the W3 bath only, at a temperature of 53°C ± 1°C, a pH-value of 4.2 ± 0.1 and with a bath volume of 65 litres.

This bath was used with air agitation and mild-steel or stainless steel substrates (panels 1 dm^2 or more).

For the acid dip corrosion tests, the stainless steel substrates were activated by a short period (20 s) with an anodic potential (3 V) and a longer cathodic period (60 s, 2 V) in a Wood nickel bath (100 g/l $NiCl_2 \cdot 6H_2O$ and 100 ml/l conc. hydrochloric acid).

For the X-ray diffraction investigations, the deposited nickel films were removed from the stainless steel substrate (the substrates were not activated) to avoid false reflections.

Pulse	I_c A/dm^2	T_c ms	I_a A/dm^2	T_{off} or T_a ms
DC	3.45	-	-	-
PC1	3.45	80	0	20
PR	3.45	40	8.63	10

Table 1: Pulse plating patterns applied to samples for corrosion and X-ray diffraction experiments.

All pulse plating was carried out using the Computer Aided Pulse Plating [4] (CAPP) system developed by the Centre of Advanced Electroplating (CAG). The system consists of a research rectifier (12 V, 20 A) and an interface to a computer performing precise programming and execution of pulse patterns.

Moist SO_2-test

A very efficient corrosion test for nickel, is the Moist SO_2-test (ASTM G 87-84). Two panels of each of the three pulse patterns from table 1, were plated with nickel from the W3 bath. In each test cycle the panels were exposed in the chamber for 8 hours at 40°C with 0.2 litres of SO_2 gas. Then they were washed, dried and evaluated according to ASTM B 537-70, and allowed to rest for remaining approximately 16 hours until the next cycle.

Nickel deposition was performed by passing the same total charge to each panel, regardless of the pulse pattern used. The average coating thickness on the panels, based on weight measurements, was 14 µm of nickel.

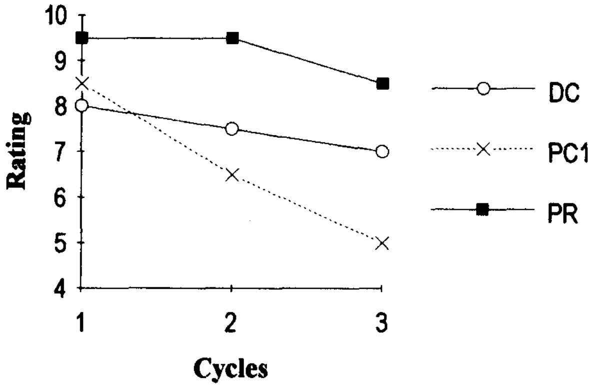

Figure 2: Result of the Moist SO_2-test. A rating of 10 corresponds to no visible red rust.

The test will determine the efficiency of the corrosion protection provided by the nickel coating. However, it is not possible with this test to distinguish between low porosity and low dissolution rate of the coating itself.

From figure 2, the difference between DC and PR nickel is obvious, while the performance of the PC coatings is a little more difficult to explain. The reasonably good result after the first test cycle, could be a result of the low porosity PC is known to have [4,7]. Later in the test however, the fast dissolution of the coating itself, rapidly creates new pores and corrosion of the base metal.

Acid dissolution test

Using different acid solutions, the dissolution of PR and DC plated nickel (see table 1) were measured as the weight loss (percentage of initial deposit weight) as a function of time (minutes in acid solution). In these experiments stainless steel was used as the substrate in order to avoid interference from dissolved substrate elements.

After 30 minutes in 7 M nitric acid, 25% of the PR deposit had been dissolved while almost 50% of the DC deposit had been dissolved. After 60 minutes the nickel coating was completely stripped off a circular area of the DC panel, while the PR panel still was free of perforations (this is also because of the improved distribution of metal caused by these pulse patterns [7]). Eventually, after 375 minutes, all the nickel on both panels had been dissolved (see figure 3).

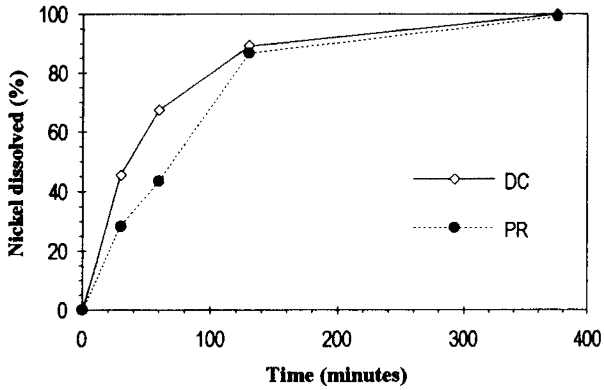

Figure 3: Nickel dissolution measured by weight loss in percentage of initial deposit weight. Samples submerged in 7 M nitric acid.

Similar experiments using a 20 g/l citric acid solution (see figure 4) and a 3 M hydrochloric acid showed that the PR plated nickel corroded significantly slower than the conventional DC deposits.

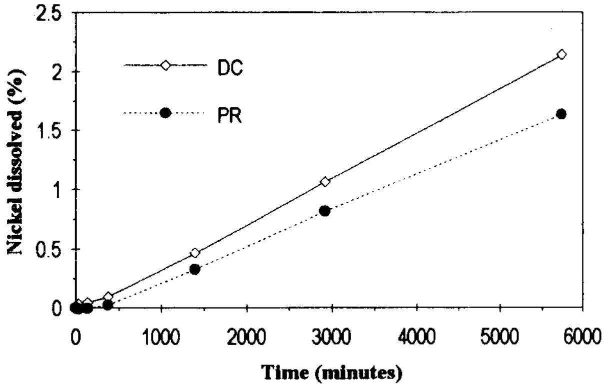

Figure 4: Corrosion performance of pulse reversal (PR) and direct current (DC) plated nickel deposits in a 20 g/l citric acid solution.

X-ray diffraction

Three films, prepared as described above, were analysed by X-ray diffraction with a Rigaku RAD-IC instrument using CuKα radiation. The angle between the incident X-ray beam and the face of the films were changed from 40.00 degrees up to 110.00 degrees to measure the diffraction patterns.

Reflection	Powder [8]	DC	PC	PR
(111)	100	100	100	100
(200)	42	33	35	72
(220)	21	53	24	4
(311)	20	21	31	24
(222)	7	5	7	4

Table 2: Texture in the Ni films. The intensities are normalised to the intensity of the (111) diffraction line.

An analysis of the film textures (see table 2) where the intensities are given in percentages of the (111) line intensity. For comparison the intensity ratios of the ASTM powder analysis [8] are shown. The PC film has intensity ratios that compare well with the powder analysis.

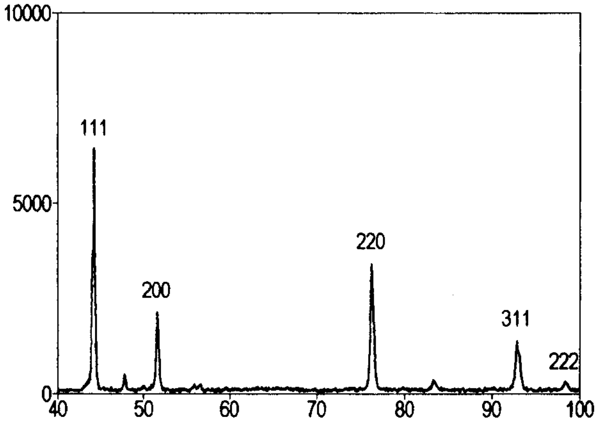

Figure 5: X-ray diffraction results for the DC nickel film. Intensity (CPS) versus 2θ measured in degrees.

This implies that the crystallites in the PC film are randomly oriented and thus the film has no specific texture. The intensities of the films DC and PR reveal significant texture as compared to the powder analysis.

For the DC film the (220) line is dominating, and for the PR film it is the (200) line that dominates.

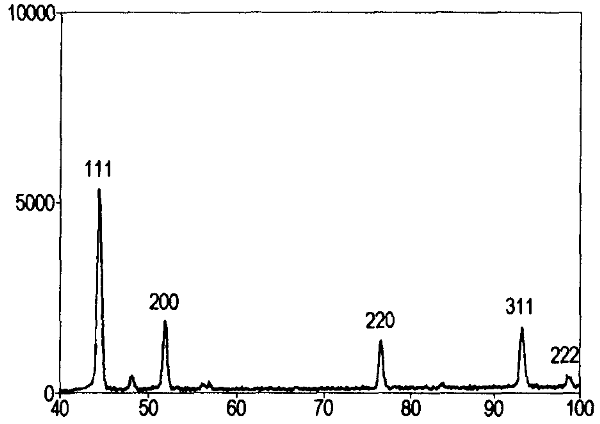

Figure 6: X-ray diffraction diagram for PC. The pattern is comparable to the distribution of powder nickel [8].

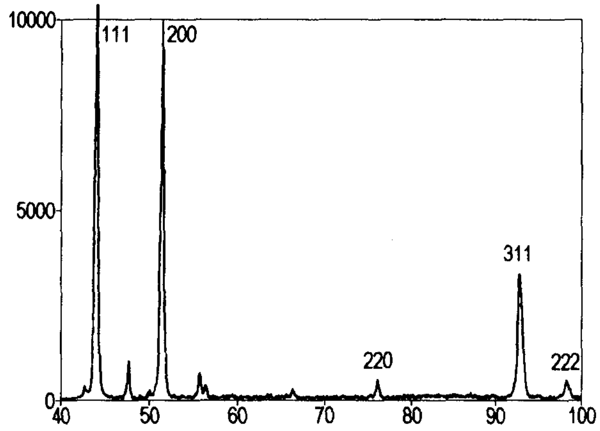

Figure 7: X-ray diffraction diagram for PR. The intensity of (220) is almost extinguished while the intensity of (200) is profound.

Considering the comparative investigation of the dissolution of DC and PR plated nickel in different acid solutions, such as nitric or citric acid, which showed a small but consistent difference, a likely explanation is that the corrosion rate for (220) crystallites (preferred orientation for DC) is generally higher than the corrosion rate of (200) which is the preferred orientation of PR.

Electroforming

The most widely used nickel bath for electroforming is the sulphamate bath. Although far more expensive than the Watts bath and relatively sensible to pollution, the advantages of sulphamate nickel, mainly speed and low internal stress, are indispensable.

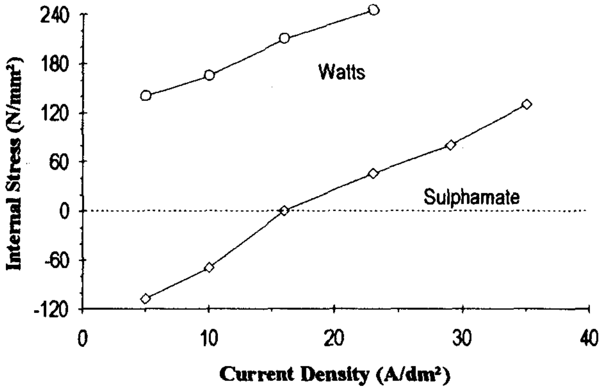

Figure 8: Internal stress versus current density (DC) for nickel deposits plated at 60°C [6].

Material distribution

High speed plating at high current densities has a serious drawback. As the current density increases the material distribution ability (or macro throwing power) decreases.

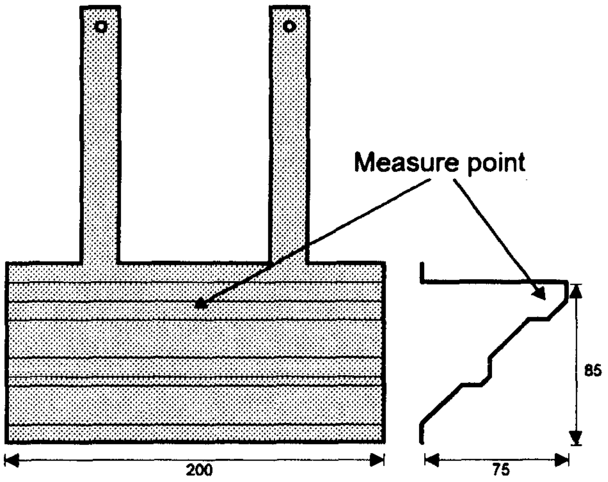

Figure 9: The shape of the test panels used for optimising the material distribution. All dimensions are in mm.

Plating complex shapes, this can result in thick deposits on corners and edges while the deposit in other areas is paper thin. Using DC plating the only way to overcome this problem of bad material distribution, is to reduce the current density.

Reducing the current density in sulphamate baths will, especially if certain additives are used, result in internal (compressive) stress. This could release the deposit from the mandrel or substrate during plating, or lead to deformation of the deposit later.

The extreme design of the test panels makes it possible to measure improvements faster, and enhances the differences between the different pulse patterns applied.

	Bath	i_a A/dm^2	T_a ms	T_c ms	Q_a / Q_c %	f Hz
1	W3	7.0	10	40	50	20
3	W1	7.0	40	112	71	7
4	W3	8.75	40	160	63	5
6	W1	8.75	20	100	50	8
7	W3	10.5	20	84	71	10
9	W1	10.5	10	48	63	17
10	Sulph.	2.0	-	-	0	-

Table 3: Extract from the experimental plan used for optimisation of the material distribution.

Given the large number of parameters, a Taguchi [4] experimental plan was designed. Selected experiments from this plan are illustrated in table 3. Variance analysis of the results (see table 4) showed that the parameters having the greatest influence on the material distribution were the ratio Q_a / Q_c and bath composition, while i_a and T_a proved to be less important. Experiment 10 was DC plating in a commercial sulphamate solution at 2 A/dm^2.

In all experiments, the test panel received a total charge of 31000 C and a cathodic current density of 3.5 A/dm^2 was used. Although the pulse plating experiments were longer in time than the DC experiment, pulse plating would reach a thickness of 1 mm at the measure point faster than with DC, because of the improved material distribution.

	Time minutes	Thickness µm	Time to 1 mm hours	Nickel to 1 mm kg
1	41	0.73	936	12.51
3	78	1.38	942	6.62
4	55	1.15	797	7.94
6	39	0.90	722	10.14
7	71	1.41	839	6.48
9	53	1.05	841	8.70
10	29	0.46	1051	19.85

Table 4: Obtained and calculated results of the experiments described in table 3. The coating thickness was measured in the point shown in figure 9.

Also the use of nickel metal can be reduced. In experiments 3 and 7 only approximately one third, as compared to experiment 10, of the nickel is necessary to provide a minimum thickness of 1 mm everywhere on the test panel.

Hardness

Electroformed parts are often used for embossing or as another type of tool. In this case, hardness plays an important role in reducing the wear of the nickel.

Sulphamate nickel is usually harder than Watts nickel, but if the chloride concentration is very high (like in solution W1) the obtained hardness is fully comparable with that of sulphamate nickels. Temperature and pH-value of the bath are also important parameters.

Bath	Plating method	Temperature °C	Hardness $HV_{0.05}$
W1	PR	30	315
W1	PR	40	292
W1	PR	50	263
Sulphamate	DC	42	276

Table 5: Average hardness values ($HV_{0.05}$) for some pulse plated nickel coatings (W1 solution) as compared to a commercial sulphamate bath.

It has been shown [9] that pulse plating using simple on/off pulses can increase the hardness of the nickel, but the increase is relatively small as long as high frequencies are avoided. A frequency higher than approximately 20 Hz can be difficult to obtain with conventional pulse rectifiers. When larger areas are involved, as for most electroforming jobs, it would be very expensive to construct a pulse rectifier capable of switching 2000 A on and off at 50 Hz or more.

Internal stress

When nickel is used for electroforming it is very important that the internal stress in the deposits is low. Internal stress around 200 N/mm^2 or more, makes the tension strong enough to seriously deform the deposit. This is not acceptable for most electroforming purposes. Internal stress has been measured using a dilatometer [10].

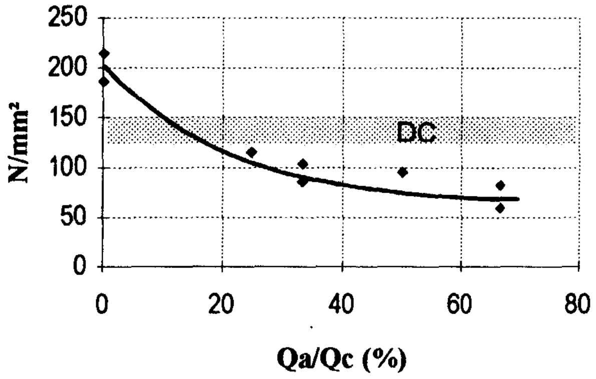

Figure 10: Internal stress (solution W2) versus the anodic to cathodic charge ratio. PC conditions exist when $Q_a / Q_c = 0$.

It has previously been demonstrated [9] that PR can reduce the internal stress in deposits from Watts based electrolytes.

Increasing the chloride concentrations in the bath, from 50 g/l (solution W2) to 300 g/l (solution W1), the internal stress becomes very high (figure 11).

Using the W1 solution the high internal stress can be reduce to almost zero by applying PR to a bath containing small amounts of a commercial additive. The stress is not reduce by the additive or by pulse plating alone. Stress free deposit can be obtained with current densities in the range from 0.5 to 7.5 A/dm^2.

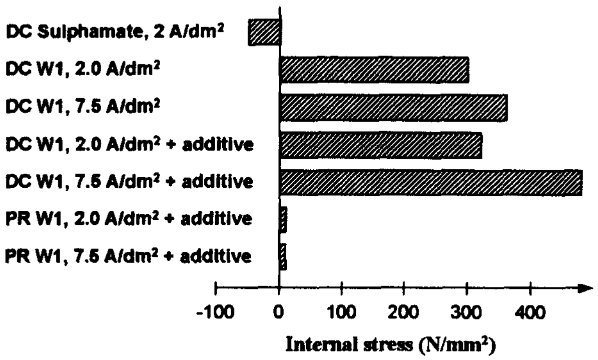

Figure 11: Internal stress in nickel deposits. PR plating was $i_a = 2.5 \times i_c$, T_c = 100 ms and T_a = 20 ms.

Summary

Corrosion protection

Comparing different types of pulse plated nickel using the moist SO_2-test, the results are seen as a combination of porosity and corrosion resistance. This makes it more difficult to determine which crystal orientation is responsible for a specific result, but some indications should be emphasised.

The PR plated samples are significantly better than DC for corrosion protection, partly because of the improved material distribution achieved through pulse reversal plating, and partly due to the shift in preferred crystal orientation from (220) to (200).

Electroforming

Other PR experiments, using almost the same pulse patterns, have been used for electroforming investigations. Watts baths with very high chloride concentrations can, with a combination of PR plating and a commercial additive, provide stress free nickel coatings with improved material distribution and the same hardness as sulphamate nickel.

Acknowledgement

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