Pulse plating of nickel from a sulfamate electrolyte.

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Abstract.

Physical and microscopical properties of nickel electrodeposited from a sulfamate electrolyte is investigated. The nickel coatings are produced using direct (d.c.) and unipolar pulsed current. Pulse reversal is not investigated because of passivation phenomena during the anodic phase.

The following properties are investigated: formation rate, current efficiency, throwing power, crystal orientation and internal stress.

The formation rate can be improved compared to conventional direct current plating, when plating is performed with square waved pulses. The current efficiency is not effected during pulse plating, if pulses superimposed on a base current are used. The efficiency decreases when high frequency pulse/pause plating is performed.

For the pulse patterns investigated in this survey, a moderate improvement in throwing power compared to d.c. plating is obtainable.

The preferred crystal orientation is [200]. In areas plated under high current field strength, the only crystal orientation beside the plane [200] is [111]. In areas plated under low current field strength, other orientations are present. It is possible with pulse current to increase or decrease the relative intensity of the various orientations. It is also possible to obtain the same crystal orientation in areas plated under high and low current field strength.

The internal stress in the outer 2-3μm of the nickel coatings is compressive. It is possible to increase or decrease the stress values, if plating is done with pulsed current.

1 Introduction.

Electroforming of metallic parts is a well established technology. With the development of the LIGA process, electroforming of micromechanic parts of metals with high aspect ratios, was made possible. Electrodeposited nickel and nickel alloys like Ni/Fe has been used for production of microactuators and micropumps.

In the LIGA process, nickel is deposited from a sulfamate electrolyte. The solubility of Ni-sulfamate is high compared to salts of chloride and sulfate. For this reason, nickel can be deposited at a high current density. Addition of chloride to the electrolyte increases the dissolution of the anodes, but it also results in a higher internal stress in the Ni-coatings. In general, additives in a sulfamate electrolyte tends to refine the grain size, increase the hardness and tensile strength, and reduce the internal stress of the coating.

The use of surface active compounds increases the complexity of the process and the need for analytical control. Furthermore, additives have been shown to break down during operation, resulting in a change of the preferred crystal orientation of the deposited nickel atoms /1/.

During d.c. plating, nickel growth is governed by several interfacial inhibitors such as H_2, H_{ad} and $Ni(OH)_2$ /2/. These inhibitors determine most of the structural and macroscopic properties of the nickel coatings. Pulse plating is thus a powerful means of influencing the adsorption-desorption phenomena occurring at the nickel/electrolyte interface.

The advantage of using pulse plating versus conventional, direct current (d.c.) plating is the strongly increased number of independent parameters controlling the deposition process. It is not only possible to improve the quality of existing plating processes, it is even possible to deposit coatings and alloys, which cannot be deposited under d.c. conditions. Furthermore, pulse plating is performed in electrolytes without or with a reduced number of additives.

The purpose of this paper is to summarize some of the results obtained with d.c. and pulse plating of nickel from a high speed sulfamate electrolyte.

Table 1. Composition of the high speed nickel sulfamate electrolyte.

Bath constituents	Concentration
Ni^{2+}	115.0 g/l
Cl^-	1.5 g/l
H_3BO_3	35.0 g/l
pH	4.00
Wetting agent*	3.0 ml/

*Na-ethyl-hexyle sulfate

2 Experimental.

The formulation of the sulfamate electrolyte is shown in table 1, consisting of analytical grade chemicals. Prior to electrodeposition, the electrolyte was treated with active carbon for 24 hours and dummy plated for 6 hours at 0.15 A/dm^2. If not otherwise stated, the plating temperature is 45°C and plating is stopped at 1200 Coulombs.

The mild steel panels have a surface area of 0.16 dm^2 and are mounted at a distance of 5 mm from a plastic board (figure 1). The panels are placed facing the anode (S-Ni rounds) at a distance of 10 cm. The thickness of the Ni-coatings are measured at the center of both sides of the panels with a Fischerscope 1550 X-ray instrument. The throwing power is expressed as the back to front ratio. The current efficiency and the formation rate is calculated on the basis of weight differences.

The test panels are investigated in a JEOL JSM-5400 LV Scanning Electron Microscope equipped with an Energy Dispersive Spectrometer from Noran Instruments. Micrographs are performed at an acceleration voltage of 20 kV in order to see the structure at the surface and to measure grain size where this is possible.

Crystal orientation is investigated with a Rigaku X-ray Diffractometer System, (Geigerflex) and the diffraction pattern between 2Θ = 40° and 100° is collected. The X-ray source is a copper anode with a wavelength λ=1.5405 Å. Intensities of the diffracted rays from the different crystal planes are compared.

Residual stress measurements in the Ni-coatings are determined with a Rigaku Strainflex with Cr Kβ radiation. The wavelength is λ=2.0848 Å and the stress results are based on the slope of the diffraction angle vs. the $\sin^2\psi$ line from [311] in the FCC crystal structure of Ni. This method is well known as the "$\sin^2\psi$ method" /3/.

The pulse patterns investigated are constructed on the basis of a Taguchi L_9 orthogonal array (see Appendix 1), and all experiments - including d.c. plating - are made as doublets. Due to passivation phenomena, pulse reversal cannot be applied in electrodeposition of nickel coatings from an additive free bath with low chloride content. Therefore, only unipolar pulses are investigated. Furthermore, two extra pulse experiments are conducted in order to evaluate the predictability of the Taguchi calculations.

In the experiments, a system called CAPP (Computer Aided Pulse Plating)/4/ is used. The CAPP system is coupled to a 5A/12V pulse rectifier built at The Technical University of Denmark. The pulse system is capable of producing pulses as short as 1 ms. The rise and fall times of the pulses are no longer than 0.1ms.

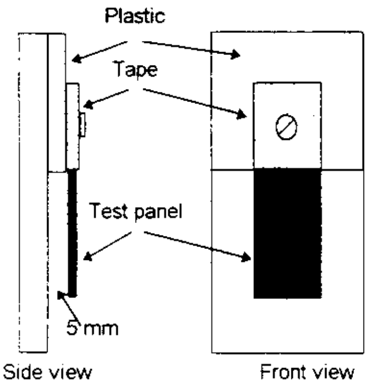

Figure 1. Mounting of the test panels.

3 d.c. electrodeposition.

The deposition rate increases linearly with the current density up 7 A/dm^2. At higher values, the total reaction mechanism is controlled by diffusion. When the current density reaches 10 A/dm^2, $Ni(OH)_2$ starts to deposit because of the increased pH of the electrolyte close to the cathode /2/.

During d.c. plating, the current efficiency is independent of the bath temperature (40 - 50 °C) and the current density (1 - 8 A/dm^2). Electrodeposition of nickel is taking place at an efficiency of approximately 99.0 per cent (figure 2).

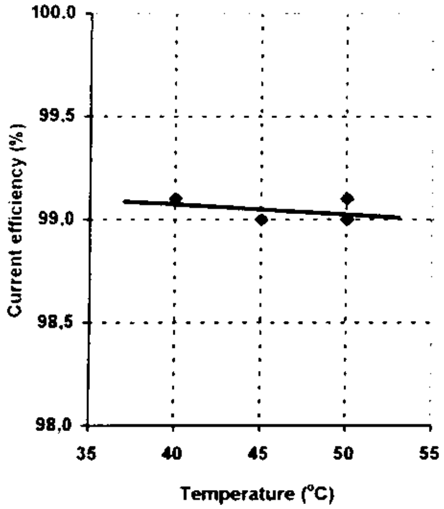

Figure 2. The current efficiency of Ni plating with d.c. current relative to the bath temperature

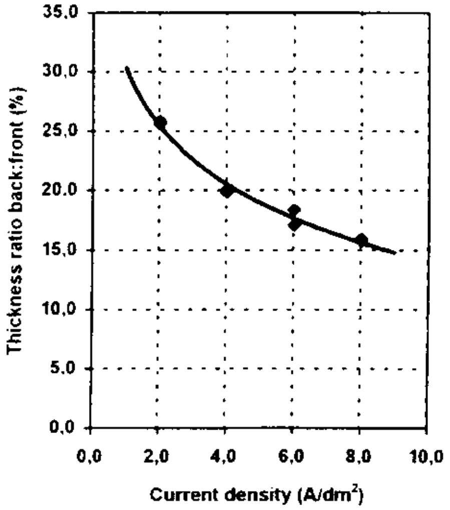

Figure 3. Throwing power for d.c. electrodeposited Ni relative to the current density

The throwing power for d.c. deposited coatings is dependent on the current density (figure 3); increasing the current density decreases the thickness ratio (back:front).

The preferred crystal orientation is the [200] plane (table 2). When plating under a high field strength (the front side of the test panels), approximately 10 per cent of the crystals have an [111] orientation. Hardly any crystals are arranged in the orientations [220], [311] and [222]. On the back side of the panels (areas plated under low field strength) a slightly greater amount of [111] oriented Ni-crystals are found. Crystals oriented according to plane [220], [311] and [222] are also present.

In relation to areas plated under high current field strength, no variation in the preferred orientations is seen in relation to the current density (table 2) and the temperature of the bath.

On the reverse side of the panels, increasing the temperature of the electrolyte results in a orientation change from [111] to [220] (figure 4).

Front of the test panels (high current density)

Current density	Crystal orientation				
(A/dm²)	[111]	[200]	[220]	[311]	[222]
2	9	100	0	1	0
4	10	100	0	1	0
6	11	100	0	1	1
8	9	100	0	1	0

Back of the test panels (low current density)

Current density	Crystal orientation				
(A/dm²)	[111]	[200]	[220]	[311]	[222]
2	13	100	5	2	1
4	12	100	1	2	0
6	13	100	1	1	1
8	18	100	1	2	1

Table 2. Crystal orientation for d.c. electrodeposited Ni coatings in relation to current density. The intensity is relative to plane [200], which is set to 100%.

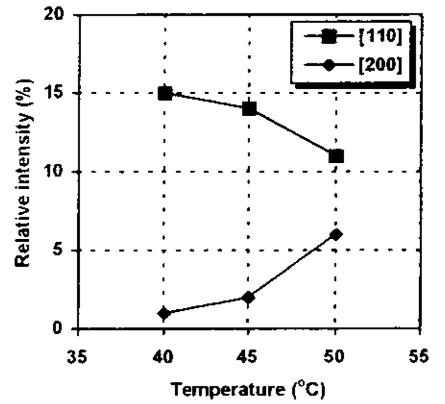

Figure 4. The relative intensity of orientation 111 and 220 in relation to the process temperature. The intensity of plane 200 is set to 100%.

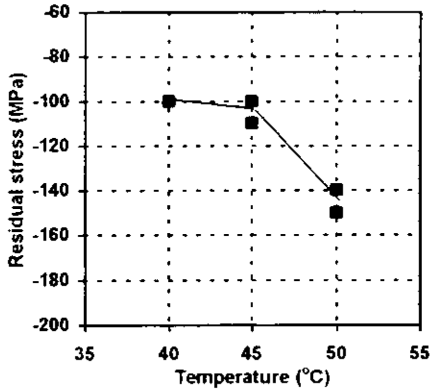

Figure 5. Residual stress in the outer 2-3µm of d.c. deposited nickel in relation to the temperature.

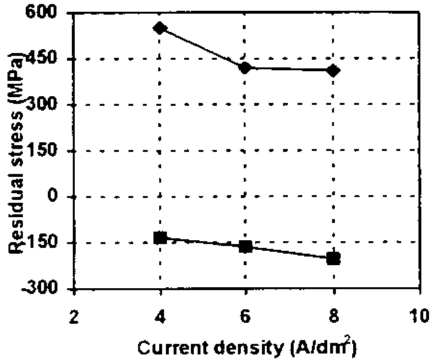

Figure 6. Residual stress in d.c. deposited nickel in relation to the current density. The upper line shows the stress in the outer 1-2 µm, and the lower line the stress in the outer 2-3 µm.

The internal stress measured in these experiments is a residual stress related to the outer 2-3µm of the coatings and cannot be compared to dilatometric measurements of the mean internal stress. Nevertheless, the measurements contain information about internal stress related to the conditions at the substrate/coating interface: the penetration of the X-rays are constant and all samples have the same thickness.

The residual stress is of compressive nature and increases with increasing process temperature (figure 5). It increases significantly at temperatures above 45°C. At temperatures above 45°C the observed increase is related to a change in the surface diffusion of adsorbed nickel atoms and/or an increased concentration of adsorbed nickel atoms because of increased diffusion from the bulk of the solution. The changes influences the nucleation process, resulting in an increased residual stress in the first deposited layer.

Increasing the current density also results in increased compressive stress (figure 6). The concentration of adsorbed nickel atoms at the surface is influenced by the rate at which the charge transfer reaction takes place /5/.

The mean internal stress measured dilatometrically depends on the coating thickness. It is known /6/ that the internal stress can change from compressive to tensile stress when current density is increased. In the outer 1-2 µm, the residual stress seems to be of tensile nature and it decreases, when the current density increases (figure 6).

Some test panels have a linear relation between the diffraction angle and the $\sin^2\psi$ line from [311] in the FCC crystal (figure 7), but others do not show this correlation (figure 8). A better correlation is obtained by splitting the measurements into a group with compressive stress (2-3 µm from the surface of the coating) and a group with tensile stress (1-2 µm).

4 Pulse plating.

Compared to electrodeposition under d.c. conditions, the formation rate can be slightly increased (< 5%) with unipolar pulses superimposed on a base current (PS). On the other hand, pulse/pause patterns results in a decreased formation rate (<9%). This is likely to be caused by a decreased concentration of

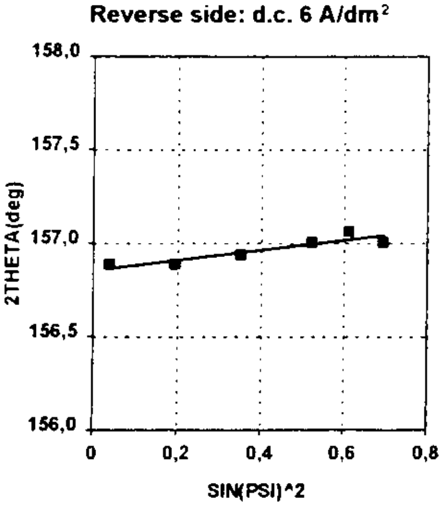

Figure 7. Diffraction angle vs. sin²ψ line from [311].

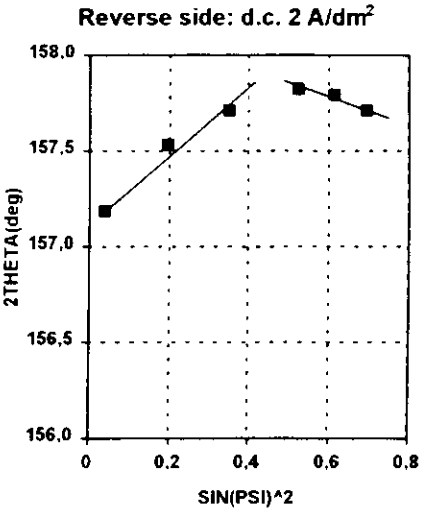

Figure 8. Diffraction angle vs. sin²ψ line from [311].

metastable Ni(I)-complex and an enrichment of adsorbed hydrogen during a pulse pause /4/;

$NiOH_{ad} + H^+ \rightarrow Ni^{2+} + H_{ad} + OH^-$ (eq. 1)

Taguchi calculations for the current efficiency supports the presence of this reaction during the pause period (figure 9); the current efficiency is lowest when i(off) = 0 A/dm².

According to the Taguchi calculations, the highest current efficiency is achieved with short pulses (10ms) of low current density (4 A/dm²) superimposed on a high base current (2 A/dm²) and separated by a period of 10 ms (duty cycle = 50%). The results of the control experiments show that the predictability for the current efficiency is fairly good. Nevertheless, the improvement relative to d.c. deposition is very moderate (<1 per cent).

Compared to d.c. plating, the largest improvement in the formation rate is a short pulse (10ms) of low current density (4 A/dm²) followed by 5 ms without current. The validity of

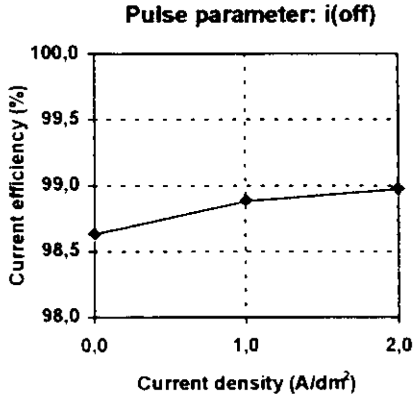

Figure 9. Current efficiency: Taguchi curve for the current density between the pulses

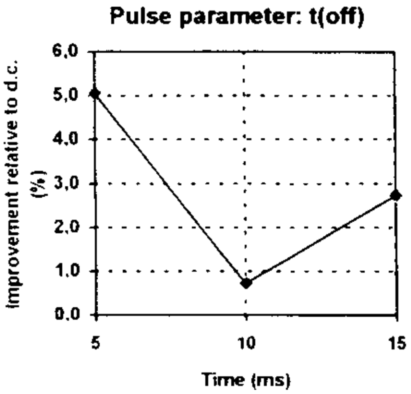

Figure 10. Formation rate: Taguchi curve for the time between the pulses

the prediction is not very good, indicating that interactions between the pulse parameters are present. This is also supported by the V-shape of the Taguchi curve for the time between the pulses (figure 10).

The Taguchi calculations show that the highest throwing power is obtained with a short pulse (10ms) of 4 A/dm² superimposed on a base current of 2 A/dm² and separated by 10 ms (duty cycle = 50%). Compared to d.c. plating, the calculations show that the throwing power of the pulse experiments can be improved slightly (4%). In order to obtain this improved throwing power, it is important not to do pulse/pause plating (parameter i(off) adjusted to level I). An ANOVA (Analysis Of Variance) shows that approximately 84 per cent of the observed variations in throwing power relative to d.c. plating can be related to this parameter. All other parameters are of less importance.

During d.c. plating, the second most intense crystal orientation is plane [111]. The relative intensity (plane [200] = 100%) of this orientation is slightly higher on the reverse side of the test panels compared to the front. Pulse plating can increase the intensity of this plane (figure 11 and 12). The increase is highest on the rear side of the test panels.

Under d.c. conditions, the intensity of plane [111] on the reverse side of the test panels is slightly higher than on the front. With pulse current, it is possible to get the same degree of crystal orientation on both side of the test panels (experiment No. 2 in table 4). Furthermore, it is possible to increase the intensity of plane [111] and [211] on the back side compared to d.c. plating (experiment No. 1 in table 3).

Plane (2 1 1) is not seen on the front side of the panels when plating is done under d.c. conditions. With pulse current it is possible to favour this orientation on both sides of the panels (experiment No. 10 in table 4).

In the pulse experiments, the residual stress in the outer 2-3µm of the coatings are also compressive (figure 13). But it is possible to plate coatings with stress values higher and lower than d.c. plated nickel. All four pulse/pause experiments resulted in a higher compressive stress than the d.c. coatings.

Taguchi calculations shows that

Pulse parameter	Level of adjustment		
	I	II	III
t(on)	-5,8	-4,1	-5,9
t(off)	-4,6	-3,7	-7,6
i(on)	-3,7	-6,6	-5,5
i(off)	-12,9	-2,4	-0,6

Table 3. Taguchi values for the throwing power. Improvement relative to d.c. plating (%). See Appendix 1 for information on the levels of adjustments.

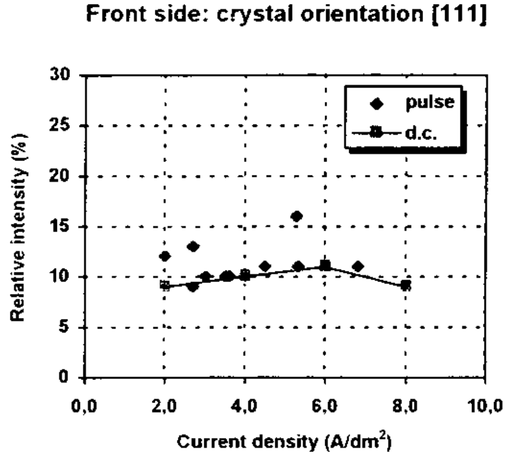

Figure 11. The front side of the test panels. The relative intensity of plane 111 for d.c. and pulse plating.

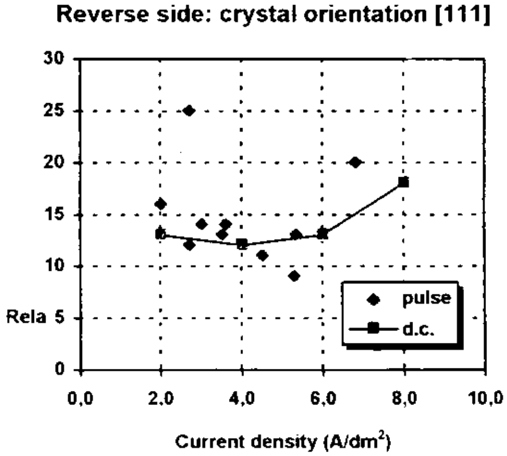

Figure 12. The reverse side of the test panels. The relative intensity of plane 111 for d.c. and pulse plating.

Experiment No.	t(on) ms	t(off) ms	i(on) A/dm²	i(off) A/dm²	Relative intensity (%) plane [111] Front/Back	plane [211] Front/Back
1	10	5	4	0	13 / 25	1 / 30
2	10	10	8	1	11 / 11	0 / 0
10	10	10	4	0	12 / 16	7 / 9

Table 4. The relative intensity of orientation [111] and [211] for three pulse experiments. Plane [200] is set to 100 %.

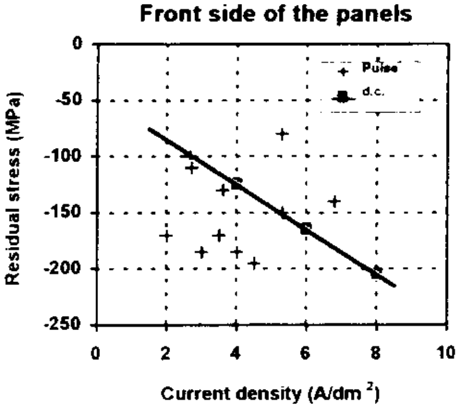

Figure 13. Residual stress in the outer 2-3μm of d.c. and pulse plated nickel.

the pulse duration (t(on) in figure 14) is of less importance. On the other hand, the pulse amplitude (t(on)) is important: increasing pulse current density results in an increased compressive stress. Increasing stress when current density increases was also observed in the d.c. plated coatings (figure 6).

The orthogonal array used assumes that there is no interaction between the parameters. But the V-shape of parameter t(off) indicates that interactions between the parameters are present. The time between the pulses is having a optimum when the base current is set to 1 A/dm^2.

A possible interaction is one between t(off) and i(off). In a period without current, results of the two control experiments. The

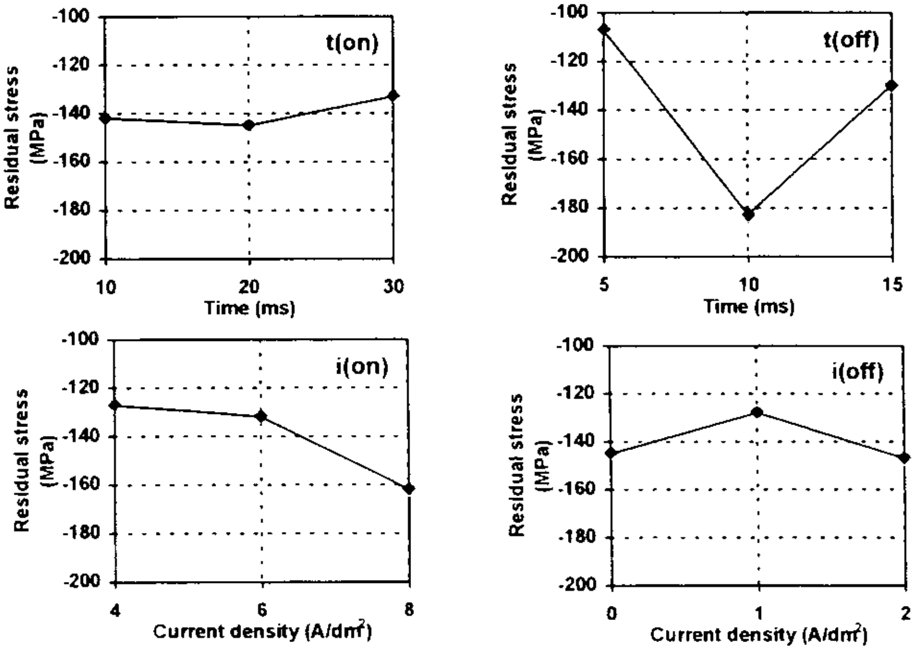

Figure 14. Residual stress of the front side of the panels: Taguchi figures for the four pulse parameters.

theoretical residual stress is up to 30 per cent lower than the measured values.

5 Conclusion.

The current efficiency is very high during nickel deposition from a sulfamate electrolyte. It is approximately 99% and is unaffeted by the bath temperature and the current density. The throwing power is very low and increasing the current density results in a large difference in thickness on the front and the reverse side of the test panels.

The preferred crystal orientation is the plane [200]. Approximately 10-15 percent of the crystals have an [111] orientation. Other orientations are only seen on the reverse side of the panels, representing areas deposited under a very low electric field strength. On the reverse side, increasing the temperature results in a change from orientation [111] to [220].

The internal stress in the outer 2-3μm is of compressive nature. Increasing the process temperature and the current density results in increased stress values.

The current densisty decreases during heigh frequency pulse/pause plating and is likely to be caused by an increased concentration of adsorbed hydrogen and a decreased concentration of metastable Ni(I)-complexes (eq. 1).

The throwing power during the pulse experiments investigated in this survey is slightly better than during d.c. plating. A significant improvement of the throwing power is to be expected during pulse/reversal plating. Because of passivation phenomena, this type of pulse pattern was not investigated.

The preferred crystal orientation of pulse plated nickel is also the plane [200]. But it is possible to increase or decrease the other planes by correct adjustment of the pulse parameters.

Pulse plating can lower the compressive stress compared to d.c. plated nickel coatings. Interactions between the pulse parameters t(off) and i(off) seems to be important. Nevertheless, the time during a pulse is not very important for the final stress values and increasing the pulse current density decreases the compressive stress.

6 References.

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Appendix 1.

The nine pulse experiments based on a Taguchi L_9 orthogonal array.

Experiment no.	1	2	3	4	5	6	7	8	9
t(on) ms	10	10	10	20	20	20	30	30	30
t(off) ms	5	10	15	5	10	15	5	10	15
i(on) A/dm²	4	8	6	8	6	4	6	4	8
i(off) A/dm²	0	1	2	2	0	1	1	2	0

Control experiments:
No. 10: t(on) = 10ms, t(off) = 10 ms, i(on) = 4 A/dm² and i(off) = 0 A/dm²
No. 11: t(on) = 30ms, t(off) = 15 ms, i(on) = 8 A/dm² and i(off) = 1 A/dm²

D.c. plating is made with the following current densities: 2, 4, 6 and 8 A/dm².