

PulsePlating

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Sample Wave Analysis

P redictions and new sciences come several ways. One might mathematically calculate boundary conditions to satisfy a possibility or discover an anomaly from data workup like Mossbauer (spectroscopy). One might symbolically dream it like Berzelius' snake eating its tail to get the structure of benzene, C₆H₆, or get divine inspiration, have "intuitive thinking" or "an educated guess based on insufficient data." All these ways have in common the desire to get to an answer. In any event, I will scrutinize some data from Nickel Sulfamate Electroforming to see if "Wave Analysis" holds any water.

Pulse Reverse Sulfamate Nickel Electroforming Several recent reports dealt with the orientation distribution function (ODF) of crystallographic texture resulting from pulse-reverse nickel electroforming.^{1, 2} The common purpose was to vary the nickel forward and reverse pulse timing to examine the relationship of ODF and coercivity (a measure of the magnetic field required to completely reverse the material's inherent ferromagnetism). The degree of [100] fiber texture produced (amount of [100] orientation density) paralleled the increased coercivity measured.

Materials with high coercivity are called "hard" ferromagnetic materials.

Electroplating of nickel has a characteristic inhibition during the process that results in the formation of various textures. These orientations from different DC conditions are [100], [110], [210] and [211]. They come about from the inhibiting effects of concomitant byproducts of plating, such as hydrogen and nickel hydroxide. An exception to this is that the absence of inhibitors allows the [100] axial growth.

Intermediate steps in nickel electroreduction involve reversible water hydrolysis to produce hydrogen ion (H⁺) plus monohydroxo-nickelate (NiOH⁺).³ (NiOH⁺) accepts an electron from the cathode and is adsorbed onto the nickel surface, NiOH_{ad}, whereupon another electron plus (H⁺) reversibly gives the adatom,

Table					
<u>ON ms</u>	<u>REV ms</u>	<u>% [100]</u>	<u>SDS</u>	DUTY*	DUTY**
2	0.5	20.17	-	0.800	0.59:
3	0.5	19.63	+	0.857	0.714
4	0.5	18.65	+	0.889	0.778
2	0.5	18.60	+	0.800	0.59:
3	0.5	17.83	-	0.857	0.714
4	0.5	17.09	-	0.889	0.778
1.2	0.5	16.60	+	0.706	0.412
5	2.0	16.38	+	0.714	0.429
5	1.5	16.31	+	0.769	0.538
5	0.5	15.30	+	0.909	0.818
5	0.2	14.12	-	0.962	0.923
5	1.0	13.11	+	0.833	0.667
5	0.8	12.82	+	0.862	0.724
5	0.5	12.82	-	0.909	0.818
5	2.0	11.10	-	0.714	0.429
10	0.5	10.65	-	0.952	0.905
5	0.8	9.16	-	0.862	0.724
5	1.5	4.30	-	0.769	0.538

 $DUTY^* = (T_{on}/(T_{on}+T_{rev}) DUTY^{**} = (T_{on}-T_{rev})/(T_{on}+T_{rev})$

Ni^o plus water before migrating to the "right spot" on the growing metallic crystal lattice.

In pulse plating nickel with high current densities and frequencies, things change slightly. A layer of colloidal nickel hydroxide forms as a result of a high localized increase in



Fig. 1—Depiction of waveforms used in studies arranged by increasing T_{on}. Shaded portions are currents. Reverse is ahead of forward.



pH near the surface.⁴ H⁺ also reduces to H^o, which can do other things besides inhibit plating, like gas off as H₂. The consumption of H⁺ causes the pH increase. The colloid layer condenses with Ni²⁺ to form micelles, ${Ni^{2+}[Ni(OH)_2]}_{colloidal}$, which produces a semi-bright to bright [211] plated appearance without the usually required additives.³ [211] did not appear as a main component in the pulse reverse work considered here.^{1, 2}

Incorporation of a reverse component in pulse plating (pulse reverse) adds the following dimension. During the reverse part of the cycle (called "off-time" in Ref. 1 & 2) the polarity reversal increases the amount of Ni²⁺ and nickel hydroxide at the surface. The Ni²⁺ helps [100] formation and nickel hydroxide is still inhibitory.

Although these explanations fit the empirical perspective, we will take a glimpse at some possible scenarios derived through examining the data. There were two different conditions of the plating bath from Ref. 1 & 2.

Conditions of Plating

The compositions used the same nickel sulfamate bath with the following exception. The later work (Ref. 2), employed the surfactant SDS (sodium dodecyl sulfate) at 200 ppm, whereas the former (Ref. 1) had no surfactant. Otherwise, the baths were composed of nickel sulfamate, 44 oz/ gal, nickel chloride, 2 oz/gal, and boric acid, 4 oz/gal. The pH was 4.2, temperature 50±1°C, and plating occurred on flat SS mandrels successively polished to 1200-graded emery and DC nickel pre-plated before pulse reverse. Pulse reverse current densities forward and reverse were the same: 223 ASF.

In both sets of experiments, the ontime (T_{on}) was held constant at 5 msec and the off-time (T_{rev}) at 0.5 msec, while the corresponding times were fluctuated. Table 1 displays the timings with % [100] orientation and whether SDS was present or not, with relative duties.

Discussion

The major difference between the two sets of data is the presence and lack of SDS and will be treated separately. The effect SDS presence compared to its lack is one of increasing the relative amount of [100] except at the least T_{on} of 2 msec. Here, the lack of surfactant allows a greater proportion of [100] (20.17 vs. 18.60). Interestingly, without SDS and holding T_{on} at 5 msec (Chart 1), there is a trend of greater diminishing [100] extending to a T_{rev} nadir at 1.5 msec, compared with SDS which reaches nadir in half that time. It would appear that SDS impedes the inhibitory effects from hydrogen and/or nickel hydroxide.

There is a parallel trend, as seen in Chart 2, whereby the presence of SDS betters [100] with constant $T_{rev} = 0.5$ msec. The T_{on} of 1.2 msec was not reported by the authors without SDS. It appears that with the greatest proportion of [100] from all data at 2 msec T_{on} and 0.5 msec T_{rev} such increasing trend without SDS could continue at lesser T_{on} and with slightly less (or more) T_{rev} .

Duty cycle doesn't relate. The only additives for the basic nickel sulfamate bath consist of SDS which is considered to be required.³

The higher concentration of nickel chloride used may be a two-edged sword. It is good for corrosion in the reverse cycle. However, it codeposits to give higher stresses and may act also to impede the plating rate as well as increase the proportion of grain orientation (crystallographic texture). Whether it should be eliminated altogether depends on many factors. What is the influence without it on the plated surface structure and on anode corrosion? Is it a sort of catalyst in plating as in acid copper? Would it be necessary to remove overplating during the reverse anodic component?

The data are limited and difficult to assess considering that half used SDS at a later date. The data also do not reflect any change in current density in that forward equals reverse and bath constituents are not varied, except that half are missing required surfactant.

The experimental conditions yielding various % [100] might be considered as sets which minimize colloid formation rather than atomic or molecular hydrogen. Varying the ratio of [H⁺]/[Ni²⁺] by substituting sulfamic acid for boric in part and then playing with Cl⁻ might give more revealing ways to alter plated nickel magnetic properties of susceptibility and remanence. Finally, it would have been nice to have had grain-size analytical results. P&SF

References

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- 4. Ref. (3), loc. cit.; ref. (2), loc. cit.