Nickel Pulse Plating From Acetate-Chloride Bath

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Acetate-chloride baths are characterized by low concentration of nickel salts: 0.3 to 0.5 mole/l. Nevertheless the deposition rate is very high due to very wide operating current density range.

Pulsing increases microhardness by about 1.5 times. Nickel coatings 9 to 12 μm thick deposited by pulsing current are practically poroless, while those 24 μm thick obtained without pulsing still have some porosity. Current efficiency is somewhat lower (85 to 92%) than in Watt's-type baths.

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Introduction

The use of nonsteady-state electrolysis such as unipolar current pulses, periodic reversal or interruptions of current is one of the ways to effect the electrocrystallization process and to obtain electrodeposits with desirable properties. For example, a combination of high and low pulses was used for the electrodeposition of microrough nickel and copper layers[1] .

Acetate-chloride nickel plating baths are characterized by low concentration of nickel salts and very wide current density range.[2] An attempt has been made in the present work to improve the properties of the coatings using pulsing current.

Experimental Procedure

Compositions of nickel plating baths are given in Table 1.

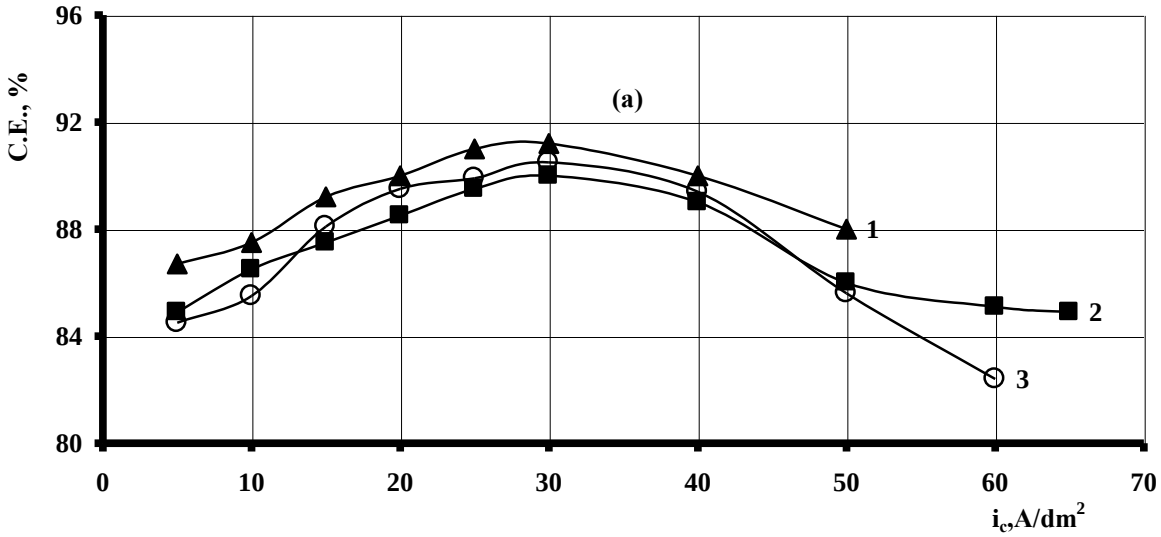
Table 1. Composition of acetate-chloride solutions

Bath #	Components of solution	Concentration		Operating conditions
		mol/l	g/l	
1	$Ni(CH_3COO)_2 \cdot 4H_2O$	0.475	118.3	t 50ºC; pH 4.5
	$NiCl_2 \cdot 6H_2O$	0.025	6.0	
2	$Ni(CH_3COO)_2 \cdot 4H_2O$	0.275	68.5	
	$NiCl_2 \cdot 6H_2O$	0.025	6.0	

Nickel chloride is a necessary bath component to improve the dissolution of nickel anodes. Cathodic pulse time, t_{on}, was equal to 1 s in all experiments and the interruption time, t_{off}, was either 0.01 s or 0.5 s. Plating experiments were carried out both with and without agitation. Two methods of agitation were used: air agitation and oscillating cathode rod in vertical direction (60 osc/min, 4 cm amplitude).

Results and Discussion

Current efficiency in acetate-chloride nickel plating solution is somewhat lower than in Watt's – type baths (Fig.1).



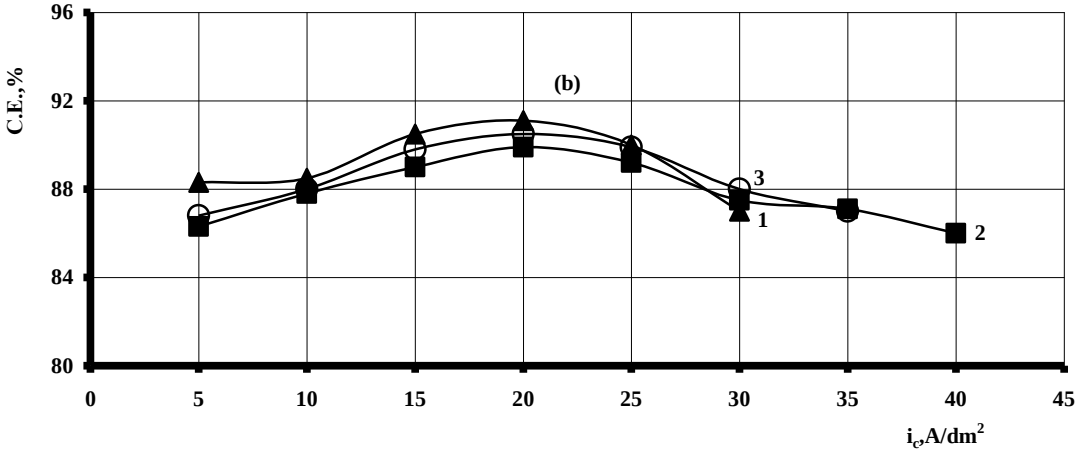


Fig.*1 Effect of current density on current efficiency during pulse plating (type II) in the bath # 1 (a) and 2 (b). Agitation mode: 1.- no; 2. –by air; 3. – by oscillating cathode rod.*

The rate of hydrogen ions discharge in Watt's-type solutions is controlled by the diffusion. Therefore partial current density for this reaction is nearly constant over a certain range of potentials. Acetate-based solutions have buffering properties. Therefore current efficiency for hydrogen evolution is in general higher than in Watt's-type baths.

There is a principal difference in the cathode processes in acetate-chloride and Watt's-type solutions at higher current densities. Hydrolyses of nickel salts and precipitation of insoluble nickel compounds takes place at higher current densities in Watt's-type solutions, thus, restricting sharply upper limit of operating current density range. On the contrary, no hydrolysis happens in the acetate-chloride solutions even at 35-60 A/dm^2.

Current efficiency for nickel is slightly decreasing at current density above 20-30 A/dm^2, nevertheless the deposition rate continues to rise up (Fig.2).

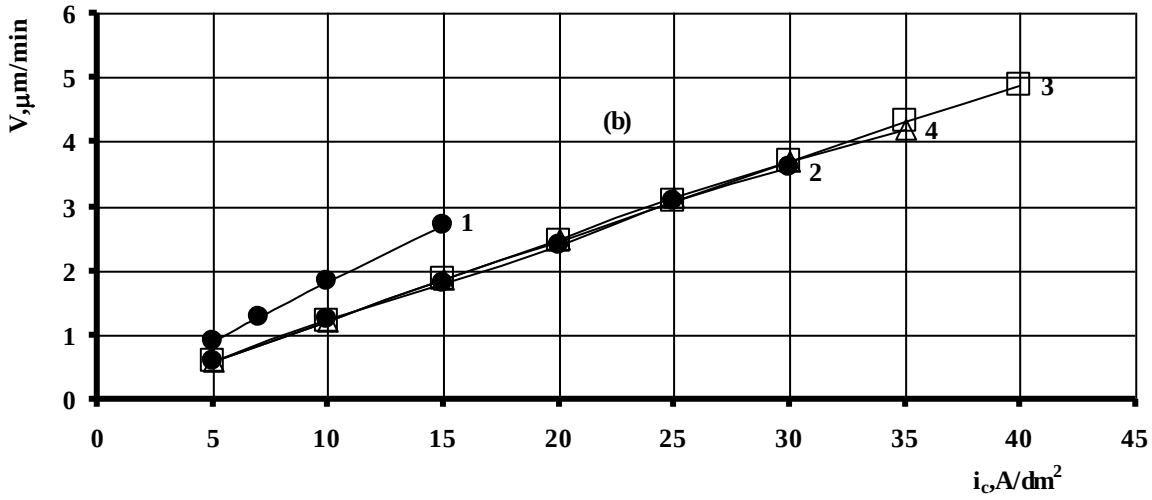


Fig.2. Effect of current density on nickel deposition rate in the bath #1 (a) and #2 (b): 1. direct current without agitation; 2,3,4 – pulse plating; agitation mode: 2. – no; 3. – by air; 4.- by oscillating cathode rod.

Deposition rate without pulsing (curves 1 in Fig. 2) is slightly higher than with pulsing.

Pulsing and method of agitation do not change the effect of current density on the deposition rate which is nearly directly proportional to the cathode current density. In the bath #1 maximum deposition rate is over 6 μm/min. Thus it takes only few minutes to deposit nickel layer of normal thickness (10-25μm).

Electrode potentials vs time in the course of the electrolysis are shown in Figs.3 and 4.

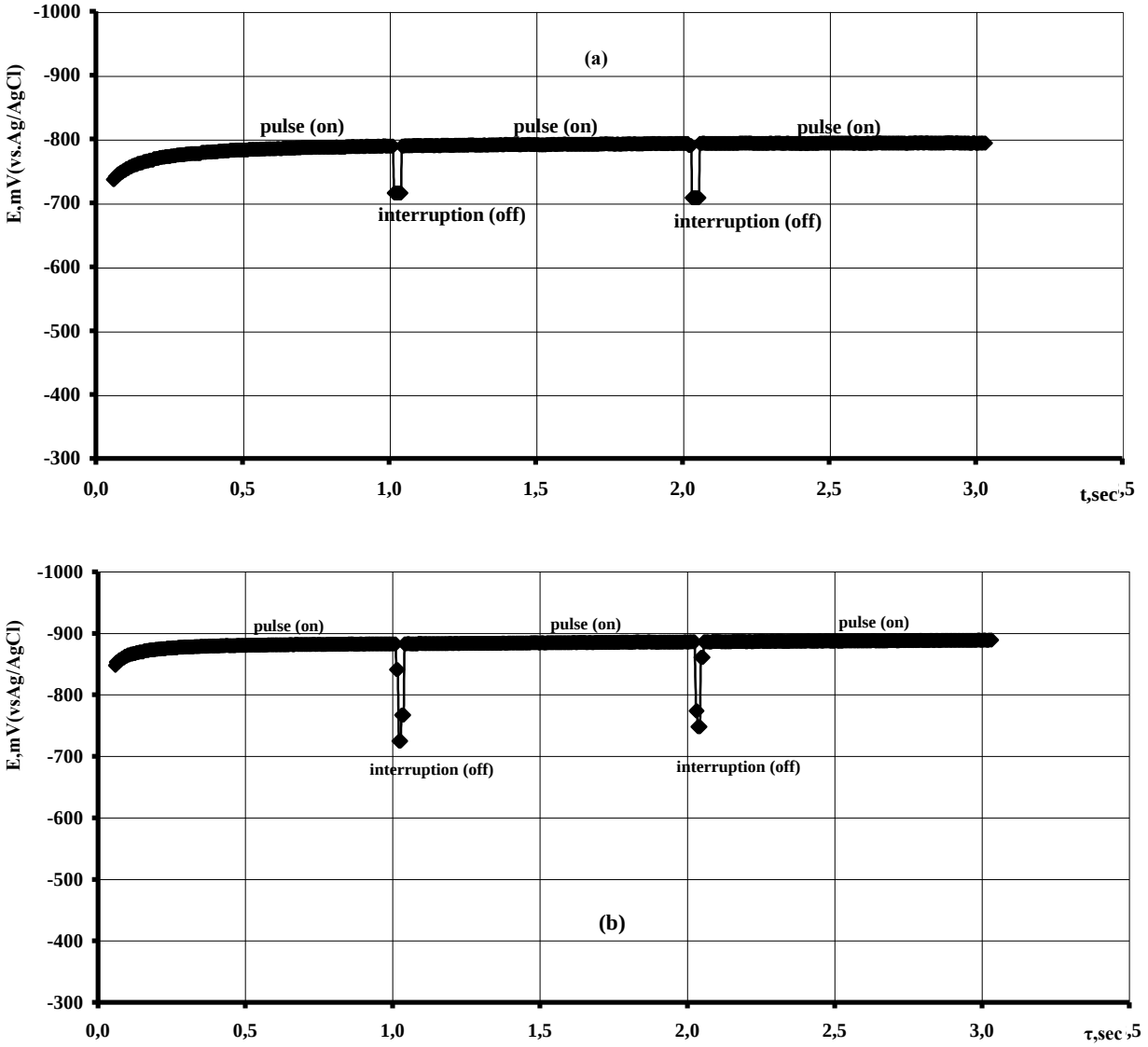
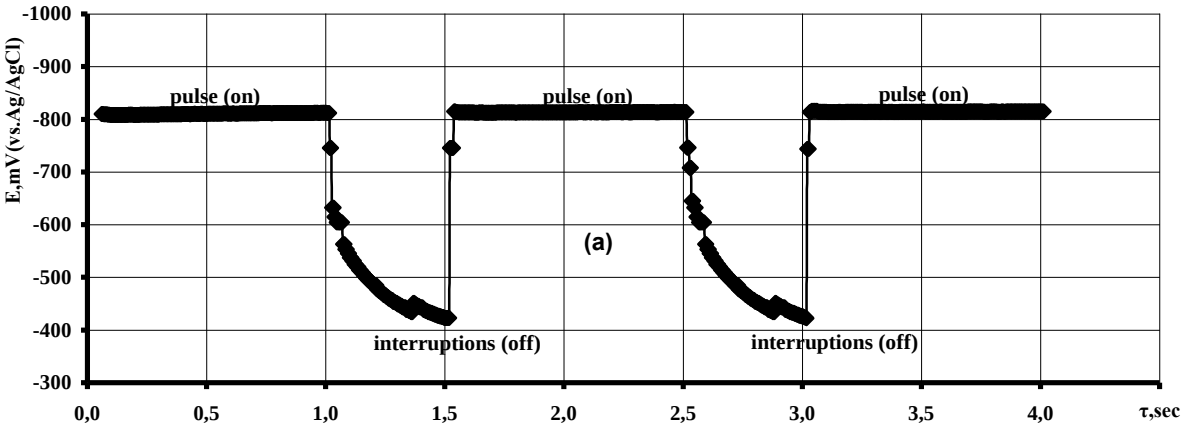


Fig. 3 Cathode potential vs time during pulse plating in bath # 2; pulse plating type I (t_{on} 1 s, t_{off} 0.01s). Current density (a) 5 A/dm^2 ; (b) 20 A/dm^2 .



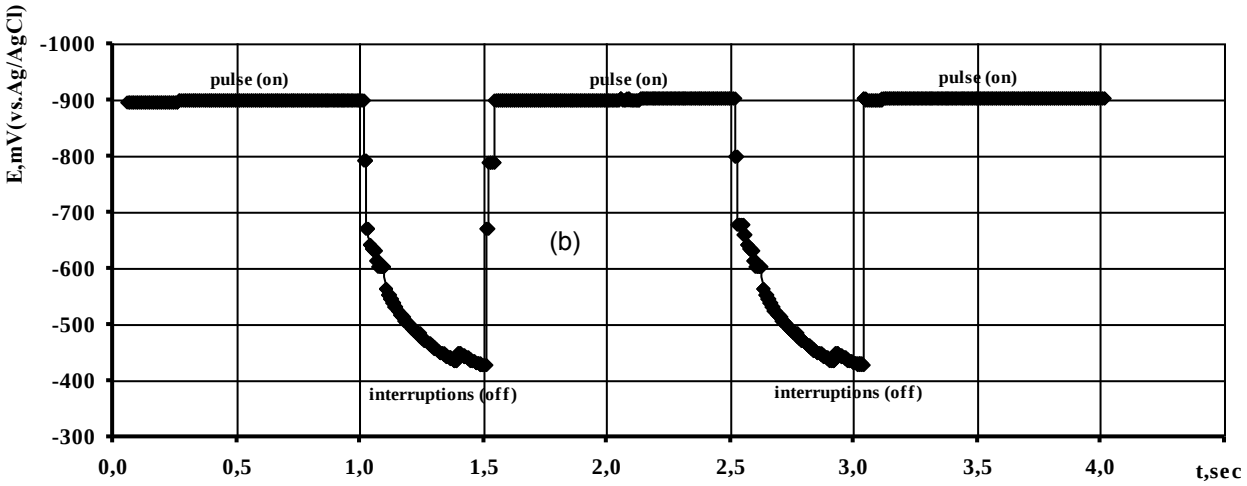


Fig.4 Cathode potential vs time in bath # 2; pulse plating type 2 (t_{on} 1 s, t_{off} 0.5 s). Current density 5A/dm^2 (a) and 20 A/d^2 (b).

In general the cathode polarization is gradually increasing along with increasing current density. A drop in the polarization after every cathodic pulse represents the discharge of the electric double layer. This process is practically invisible in curves in Fig.3 due to very short interruptions – only 0.01 s, while for longer ones – 0.5 s – the discharge process is obvious (Fig.4).

Periodic discharge of the electric double layer means interruptions in the electro-crystallization followed by the formation of new crystallization sites. Another process is related with adsorbed hydrogen which is electrochemically active and may be ionized during the interruptions (so called pseudo-capacitance). These two effects of pulsing are possible explanations of positive consequences of pulsing: elimination of pores and pitting in nickel coatings and improvement in the mechanical characteristics.

Nickel coatings deposited by pulsing current are practically poroless at thicknesses of 10 to 12 μm. Microchardness is about 1.5 times of that obtained without pulsing: coatings obtained in the bath #1 have hardness of 3.2 to 4.3 GPa, while those deposited from the bath #2 have hardness of 2.0 to 3.5 GPa.

Conclusions

1. Pulsing results in the formation of semi-bright coating over wide range of cathode current densities – up to 30-50 A/dm^2.
2. Current efficiency is relatively high – 85 to 90%
3. Pulsing eliminates pitting, reduces porosity and increases hardness of the coatings.

References

1. S. S. Kruglikov, P. Becker, and O.Jankovski, Plating Surf. Finish., 2002, vol. 89, # 3, p.45.
2. N.V. Peganova., T.E. Tsupak, Гальванотехника и обработка поверхности (Electroplating & Surface Treatment), 2007, vol. XV, no. 4, p.18.

