

# The effect of additives on the pulsed electrodeposition of copper

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The pulsed electrodeposition of copper has been systematically investigated from a copper sulphate bath. Pulse duty cycles of 5–80%, at frequencies from 10 to 100 Hz with current densities ranging from 2.5 to 7.5 A dm<sup>-2</sup> were employed. The influences of pulsed current duty cycle, peak current density and frequency on the thickness and hardness of the copper deposit, current efficiency and throwing power of the plating process were studied. The effect of additives, polyethylene glycol and di-sodium EDTA on the properties of deposit were investigated.

**Keywords:** Pulse plating, Copper, Duty cycle, Frequency, Current efficiency, Throwing power

## Introduction

Pulsed current electrodeposition<sup>1</sup> has received much attention in recent years in order to improve the mechanical and chemical properties of deposits. The advantages of pulse plating are numerous, such as the reduction of porosity,<sup>2</sup> lower gas content,<sup>3</sup> high purity, fine grained deposits and deposits having low electrical resistance.<sup>4–6</sup> It is also possible to produce harder, pore free and nanosized deposits by pulse plating.<sup>7–9</sup>

In direct current plating, only one electrical parameter is variable, the current or potential. In pulse plating an interrupted current or potential is used. The current may or may not drop to zero between pulses. Three parameters are independently variable in practical pulse plating; pulse current, pulse on-time and pulse off-time, which determine the physical characteristics of the deposits obtained from the given electrolyte.

The effect of additives on the kinetics of copper deposition has already been published by the authors.<sup>10</sup> Intensive studies were carried out on pulse electrodeposition of copper from various acid and alkaline baths with and without additives and the effect of pulse parameters on the structural properties of the copper deposits has been studied in detail.<sup>11–28</sup> Whereas much work has been carried out on the effect of various organic additives on the properties of copper deposits formed by DC electrodeposition,<sup>29–35</sup> very few data are available concerning the role of organic additives on pulsed electrodeposition and on the properties of electrodeposits.<sup>36</sup>

In the present study, a systematic investigation of copper deposition from an acid copper sulphate bath has been undertaken with the application of square wave pulse current. The influences of pulse conditions on current efficiency, throwing power and hardness have been studied in detail.

## Experimental

An electrolyte consisting of 240 g dm<sup>-3</sup> CuSO<sub>4</sub>.5H<sub>2</sub>O and 52.5 g dm<sup>-3</sup> of 1.84 SG H<sub>2</sub>SO<sub>4</sub> with polyethylene glycol and the di-sodium salt of ethylenediamine tetraacetic acid (EDTA) as additives was prepared and purified by charcoal treatment and dummied at 0.5 A dm<sup>-2</sup>. Deposition of copper was on copper cathodes (20 cm<sup>2</sup> area). The procedure used for copper plating is given in Table 1. Pulse plating was carried out at 35°C using 1 dm<sup>3</sup> of the electrolyte and employing rolled electrolytic copper anodes. Pulse frequencies ranging from 10 to 100 Hz and duty cycles ranging from 5 to 80% were used. Table 2 lists the various pulse parameters used.

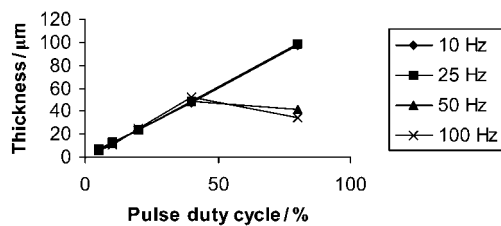
The throwing power of the copper plating bath was determined using a Haring–Blum cell. This is a long and narrow cell in which two cathodes are placed on two sides of the anode at a distance ratio of 5:1. The area of copper anode and copper cathodes is 7 × 7 cm. The panels were mechanically polished, degreased using acetone, cleaned using an alkaline solution, washed and pickled with 10% H<sub>2</sub>SO<sub>4</sub>, washed in tap water, rinsed with distilled water and dried. The unwanted sides of the panels were masked. Of the two cathodes, one panel is very near to the anode and the other is far from it (distance ratio *L*). The throwing power experiments were carried out at various frequencies and duty cycles at constant temperature (30°C). The current density was kept constant (2 A dm<sup>-2</sup>). The panels were taken out washed, rinsed, dried and weighed.

**Table 1** The general procedure for copper plating operations

1	Mechanical finishing
2	Solvent degreasing
3	Acid cleaning
4	Tap water washing
5	Rinsing in de-mineralised water
6	Plating
7	Washing
8	Rinsing

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1 Effect of pulse duty cycle at various frequencies on the thickness of the copper deposit

The percentage throwing power can be calculated from equation (1).

$$\text{Percentage throwing power} = \frac{L - M}{L + M - 2} \times 100 \quad (1)$$

where  $L$  is the linear distance ratio and  $M$  is the metal ratio. These are defined as

$$\text{Linear ratio } (L) = \frac{\text{Distance of a cathode}}{\text{Distance of near cathode}} \quad (2)$$

$$\text{Metal ratio } (M) = \frac{\text{Weight of deposit on near cathode}}{\text{Weight of deposit on far cathode}} \quad (3)$$

The hardness values of the copper deposits were measured using a LECO microhardness tester in Vickers pyramid number. Current efficiency of the pulse copper plating bath was also determined.

## Results and discussion

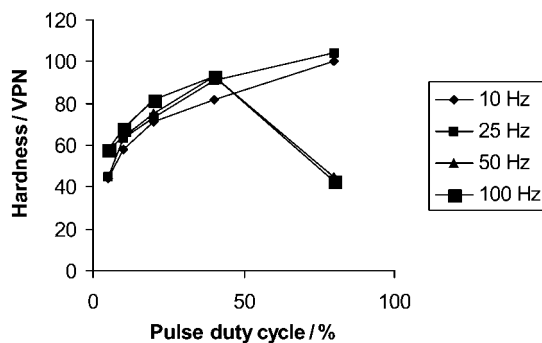
### Effect of pulse duty cycle

#### Influence on thickness

Figure 1 shows the effect of the pulse duty cycle on the thickness of the copper deposits obtained at various frequencies. From this figure, it is observed that the thickness of the copper deposit increases with increase in pulse duty cycle. As the duty cycle increases, current on-time increases and off-time decreases. At a lower duty cycle, the peak current is flowing for less time and so the overall amount of deposition is less than for a higher duty cycle. Also at very high duty cycles and high frequencies the pulse current is very low, and so a correspondingly reduced thickness is obtained. The maximum thickness was obtained at 80% duty cycle for lower pulse frequencies (25 and 50 Hz) and at 40% duty cycle for higher frequencies (75 and 100 Hz) at a current density of  $2 \text{ A dm}^{-2}$ .

#### Influence on hardness

Figure 2 shows the effect of pulse duty cycle on the hardness of the copper deposits obtained at various frequencies. The hardness of the copper deposit is found to increase with increase of duty cycle.<sup>37</sup> A maximum



2 Effect of pulse duty cycle at various frequencies on the hardness of the copper deposit

hardness value is obtained at 80% duty cycle at low frequencies (10 and 25 Hz) and at 40% duty cycle at high frequencies (75 and 100 Hz) at constant current density of  $2 \text{ A dm}^{-2}$ . Because in a low pulse duty cycle a higher peak current is passed, this produces powdery or burnt deposits with poor adhesion and considerable porosity. This porosity leads to a decrease in hardness of the deposit. However, at higher duty cycles, the peak current is lower almost nearing the optimum average current resulting in the formation of a smooth fine grained deposit. Improved surface coverage with denser build-up of grains is to be expected.

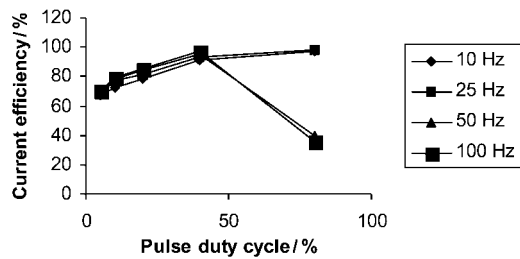
At higher frequencies (75 and 100 Hz), the pulse current appears to be almost equal to that of DC because there is not sufficient relaxation time for the re-establishment of equilibrium between the ions in the bulk solution and the surface, which leads to more hydrogen evolution that in turn leads to the formation of a porous deposit. So hardness of the deposit decreases beyond 40% duty cycle in the case of high frequency pulse plating.

#### Influence on current efficiency

The influence of pulse duty cycle on the current efficiency of the copper plating at various frequencies is shown in Fig. 3 and the values are given in Table 3. It was found that as the pulse duty cycle increases, the current efficiency of the copper deposition increases. The current efficiency can be affected by co-deposition of hydrogen at the cathode during plating. At higher duty cycles the effect is pronounced and hence lower current density is observed. Maximum increase in current efficiency has been observed at 80% duty cycle for the low frequency pulse plating and at 40% duty cycle for the high frequency pulse plating at the average current density of  $2 \text{ A dm}^{-2}$ . Increase in current efficiency must be due to the preferential reduction of an adsorbed monolayer of  $\text{Cu}^{2+}$  with pulses of charges equivalent to the reduction of this monolayer. Hydrogen evolution

Table 2 Pulse parameters used for pulse plating of copper

Duty cycle/%	Pulse frequency/Hz and pulse on-off times/ms				Current density/ $\text{A dm}^{-2}$	
	10	25	50	100	Peak	Average
5	5-95	2-38	1-19	0.5-9.5	50, 100, 150	2.5, 5.0, 7.5
10	10-90	4-36	2-18	1-9	25, 50, 75	2.5, 5.0, 7.5
20	20-80	8-32	4-16	2-8	12.5, 25, 37.5	2.5, 5.0, 7.5
40	40-60	16-24	8-12	4-6	6.25, 2.5, 18.25	2.5, 5.0, 7.5
80	80-20	32-8	16-4	8-2	6.25, 0.5, 18.25	2.5, 5.0, 7.5



3 Effect of pulse duty cycle at various frequencies on the current efficiency of the copper deposit

occurs preferentially after consumption of this monolayer and thus current efficiency decreases for increasing pulse duty cycle in the case of high frequency pulse plating.<sup>38</sup>

**Influence on throwing power**

Figure 4 shows the effect of pulse duty cycle on the throwing power of the pulse copper plating bath at various frequencies. From the figure, the throwing power increases with increase of pulse duty cycle. A maximum throwing power is obtained at higher duty cycle (80%), because at a lower duty cycle, the off-time is very high, the established steady-state concentration gradients are disturbed, and uniform deposition cannot be expected.

On the other hand at higher duty cycle, the off-time is sufficiently short to maintain a uniform distribution of metal ions from the bulk of the electrolyte to peaks and crevices of the cathode surface which leads to uniform deposition over the entire surface irrespective of the shape and size. So, throwing power is very high for pulse plating with higher duty cycle, a maximum throwing power obtained at 80% duty cycle at all frequencies for the applied current density of 2 A dm<sup>-2</sup>.

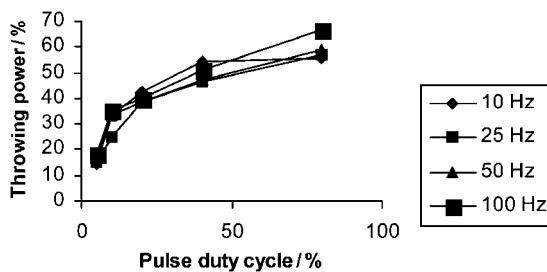
**Effect of pulse frequency**

**Influence on thickness of deposit**

The thickness of the copper deposit is found to be increase with increase in pulse frequency (Fig. 1) at all duty cycles except 80%. At 80 % duty cycle the thickness values are found to increase only up to the frequency of 50 Hz and beyond that a decreasing trend is observed. At high frequencies, short pulses with extremely thin pulsating diffusion layers are produced, so the rate at which the metal ions can be transported to the cathode interface increases, which leads to increases in nucleation rate. Thus, the thickness of the deposit increases with increase of pulse frequency. However at very high frequency and very high pulse duty cycle, diffusion of the metal ions from the bulk solution may not be

Table 3 Influence of pulse duty cycle on current efficiency of pulse plating of copper at various frequencies

Pulse duty cycle/%	Current efficiency/%			
	10 Hz	25 Hz	50 Hz	100 Hz
5	67.5	68.43	68.43	78.43
10	72.58	77.12	78.18	78.18
20	18.18	81.03	84.50	85.71
40	91.54	93.3	95.07	96.83
80	96.83	98.54	39.26	35.25



4 Effect of pulse duty cycle at various frequencies on the throwing power of the copper deposit

effective. So, although the rate of deposition is very fast, the resulting deposits are burnt and powdery in nature, which leads to a decrease in thickness of the deposit at high frequencies and very high duty cycle.

**Influence on hardness**

From Fig. 2 it can be inferred that as pulse frequency increases the hardness is also found to increase. During short pulses at higher frequency, a very thin pulsating diffusion layer is formed, which leads to an enhanced nucleation rate and surface coverage with denser building up of fine grained deposits. This leads to lower porosity and correspondingly higher hardness values are obtained. Maximum hardness was obtained at a frequency of 100 Hz for the current density of 2 A dm<sup>-2</sup>. Here also at a very high duty cycle (80%) and at a very high frequency (100 Hz), lower hardness values were obtained. This was due to the formation of powdery and porous deposits.

**Influence on current efficiency**

As shown in Fig 3, it was found that current efficiency increases with increase of pulse frequency. As pulse frequency increases, the pulses are very short and they produce very thin pulse diffusion layers. Thus transport and diffusion of metal ions from bulk electrolyte to the cathode surface through these layers is possible and much easier than through the thick diffusion layers that are obtained at low frequency or with larger pulses. So this enhancement of migration of ions increases the nucleation rate, uniformity, deposition rate and so increases the current efficiency. At 100 Hz and 80% duty cycle, lower current efficiency was obtained for the same reasons as given in the effect of frequency on thickness and hardness of the copper deposits.

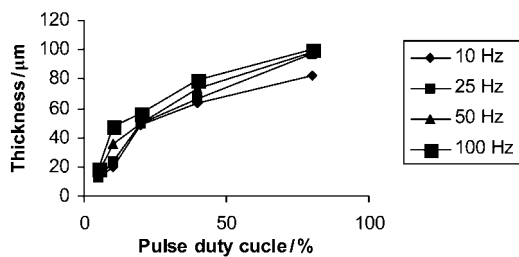
**Influence on throwing power**

Throwing power is found to increase with increase in pulse frequency as shown in Fig. 4 as short pulses (higher frequency) ensure uniform distribution of metal ions from bulk electrolyte to peaks and valleys of the surface through the very thin pulsating layers. The deposition takes place uniformly irrespective of cathode shape and geometry, which leads to higher throwing power. Maximum throwing power was obtained at 100 Hz for 80% duty cycle and at a current density of 2 A dm<sup>-2</sup>.

**Effect of pulsed current density**

As pulsed current density increases, the rate of nucleation and hence deposition increases. So all the properties of the deposition such as thickness, hardness, current

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5 Effect of pulse duty cycle at various frequencies on the thickness of the copper deposit in the presence of PEG

efficiency and throwing power were found to increase with increase of pulse current density. The reason for the improved properties is the same as explained in the effect of pulse duty cycle.

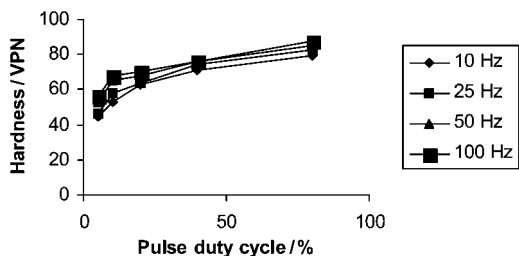
This pulse current density is proportional to the concentration gradient in the pulsating layer during pulses. Higher pulsed current density enhances the total deposition overpotential so a larger free energy is available for deposition of uniform fine grained deposit. So, higher values of thickness, hardness, current efficiency and throwing power are obtained at higher pulsed current density rather than at lower pulsed current density.

### Effect of average current density

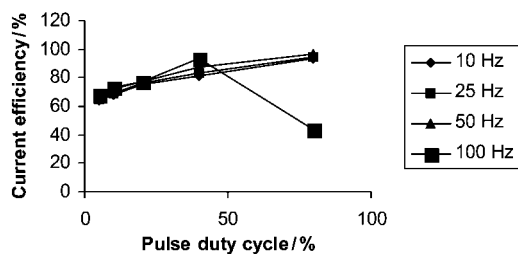
In pulse plating especially at higher frequencies, there may be two different diffusion layers; one near the cathode surface layer called the pulsating layer, and the other adjacent to this, which is essentially stationary after a number of pulses have been applied. The inner pulsating diffusion layer thickness corresponds to pulsed current density and the outer stationary diffusion layer corresponds to average current density. This average current density is proportional to the concentration gradient in the stationary layer. The thickness of this stationary diffusion layer is an important variable in determining the rate of electrodeposition process. If the thickness of this layer is less, then diffusion of metal ions from the bulk electrolyte to the cathode surface will be enhanced. At very high current densities the thickness of this layer is very high, so the ion transport through this layer is lower, which leads to lower deposition rate and deposits with poor quality are obtained. Maximum values of good quality deposits are obtained at  $2 \text{ A dm}^{-2}$ .

### Effect of additives (polyethylene glycol and di-sodium EDTA)

Additions of polyethylene glycol (PEG) and di-sodium EDTA to the copper plating electrolyte have no

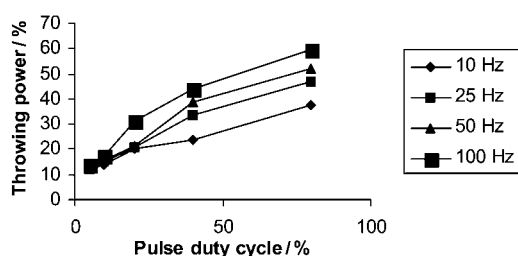


6 Effect of pulse duty cycle at various frequencies on the hardness of the copper deposit in the presence of PEG

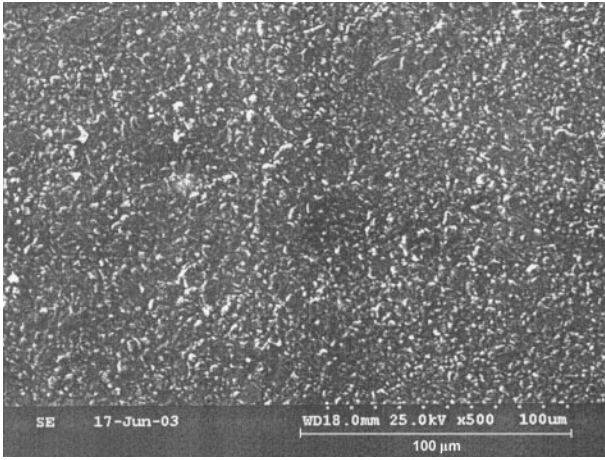


7 Effect of pulse duty cycle at various frequencies on the current efficiency of the copper deposit in the presence of PEG

significant effect on the properties of the copper deposit. Both additives have a similar effect in the pulse plating of copper, i.e. there is no remarkable difference in the properties of the copper deposits. Their combined effects on thickness, hardness, current efficiency and throwing power of the copper deposit are shown in Figs. 5–8 respectively. There are slight increases in thickness, hardness, current efficiency and changes in throwing power, but the smoothness and brightness of the deposit increase to a larger extent. The electrodeposition of copper in the acid copper bath with organic additives may be explained on the basis of the ability of the hydroxide ion to adsorb on to the electrode surface or to form complexes with the depositing metal ions. According to electrobrightening theory, a bright coating is said to be produced when a layer of colloidal particles formed near cathode is captured by a catalytically generated hydrogen film. Because of the linear form of PEG and di-sodium EDTA, they are easily adsorbed on the cathode and thus increase the cathodic polarization, which can facilitate catalytic generation of hydrogen, necessary for the production of bright coatings. It is well known that pulse deposition reduces the crystallite size that results from high current used in the pulsed electrodeposition. During the cathodic polarisation, all the cupric ions in the vicinity of the electrode are discharged and deposited, which causes a high cathodic potential resulting in increased formation of nuclei. Moreover, addition of complex formers such as PEG and di-sodium EDTA increase the rate of nuclei formation and so enhance the rate of deposition and thickness of the copper deposits. Of the two additives, di-sodium EDTA has a more pronounced effect on brightness of the deposit than PEG. Since di-sodium EDTA has two free electron pairs (amino groups) and four hydrophilic carboxylic groups, it can be a strong complex former and hence the rate of nucleation increases, which in turn enhances the thickness, current efficiency and throwing power of the bath. Since fine



8 Effect of pulse duty cycle at various frequencies on the throwing power of the copper deposition in the presence of PEG

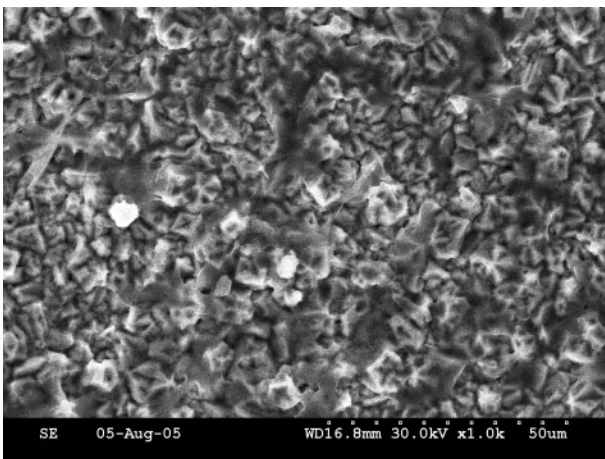


9 SEM micrograph of copper deposit obtained at 80% duty cycle and 100 Hz

grained copper deposits are obtained by the addition of these complex formers, hardness values were also found to increase.

### Scanning electron microscope (SEM) analysis

The surface morphology and porosity of the copper deposit formed by pulse plating were studied by SEM analysis. Figure 9 is the SEM micrograph of copper deposits obtained at 80% duty cycle and at 75 Hz and Fig. 10 is that of copper deposit obtained at 20% duty cycle at 10 Hz. On examining the two figures, it was found that the SEM image of the copper deposit formed by pulse plating at 20% duty cycle and 10 Hz has a higher number of pores compared to that formed at 80% duty cycle and 75 Hz, which has extremely very few pores. Also, the more uniform copper deposits obtained at a higher duty cycle and frequency have higher surface density than that of copper deposited with low frequency and low duty cycle pulse plating, so here the porosity of the deposit is very much decreased. The grain size of the copper deposit formed at high frequency and duty cycle is smaller compared to that of low frequency and low duty cycle pulse copper deposit.



10 SEM photograph of copper deposit obtained at 20% duty cycle and 10 Hz

## Conclusions

Pulse electroplating of copper on copper substrate was carried out from an acid copper bath at various pulse duty cycles, frequencies and current densities without and with additives such as polyethylene glycol and the di-sodium salt of EDTA. The pulse plating conditions such as on-time, off-time, duty cycle and frequency were optimised. The properties of the copper deposits such as thickness and hardness obtained from the bath without and with additives were evaluated. The throwing power and current efficiency of the baths were also determined. The influence of pulse duty cycle, pulse frequency, peak current density, average current density and addition agents on the properties of the copper deposit has been studied in detail. From the data obtained, it may be concluded that good quality copper deposits can be obtained at 80% duty cycle, at frequency 75 Hz and current density  $2 \text{ A dm}^{-2}$ .

## References

1. N. Ibl, J. C. Puipe and H. Angerer: *Surf. Technol.*, 1978, **8**, 287.
2. Y. Y. Wang, C. S. Tung and C. C. Wan: *Met. Fin.*, 1980, **78**(9), 21.
3. C. A. Snavey: *Trans. Electrochem. Soc.*, 1947, **92**, 537.
4. N. Ibl: *Surf. Technol.*, 1980, **10**, 81.
5. Ch. J. Raub and A. Knodler: *Plat. Surf. Fin.*, 1978, **65**(9), 32.
6. N. M. Osero: *Plat. Surf. Fin.*, 1986, **73**(3), 20.
7. W. Patteh: *Gallvanotechnik*, 1980, **71**, 107.
8. G. Devaraj, S. Guruviah and S. K. Seshadri: *Mater. Chem. Phys.*, 1990, **25**, 439.
9. P. T. Tang, T. Watanabe and J. E. T. Anderson: *J. Appl. Electrochem.*, 1995, **25**, 83.
10. C. Rajeswari, J. Bakkialakshmi, S. Mohan and N. G. Renganathan: in 200th Electrochemical Society Meeting, Extended Abstracts, September 2001, Abstract No. 644.
11. K. I. Popov: *Surf. Coat. Technol.*, 1988, **34**, 60.
12. M. Datta and D. Landolt: *Electrochim. Acta*, 1982, **27**, 385.
13. D. Tanchin and H. Zhang: *Electrochim. Acta*, 1986, **31**, 299.
14. S. Roy and D. Landolt: *J. Appl. Electrochem.*, 1997, **27**, 299.
15. D. Eliadis and R. C. Alkire: *J. Electrochem. Soc.*, 1998, **145**, 1218.
16. P. E. Bradley and D. Landolt: *Electrochim. Acta*, 1999, **45**, 1078.
17. M. S. Moats, J. B. Hiskey and D. W. Collins: *Hydrometallurgy*, 2000, **56**, 255.
18. J. P. Healy and D. Pletcher: *J. Electroanal. Chem.*, 1998, **338**, 155.
19. D. Papanayiotou and R. C. Alkire: *J. Electrochem. Soc.*, 1998, **145**, 3016.
20. J. J. Kelly and A. C. West: *J. Electrochem. Soc.*, 1998, **145**, 3476.
21. M. Fonsetti, I. Zucchi and C. Trabaneli: *Electrochim. Acta*, 1998, **44**, 311.
22. N. Tabakova, N. Pelkova and J. Stejskal: *J. Appl. Electrochem.*, 1998, **2**, 1083.
23. E. Toth-Kadar, L. Peter, T. Becsei, J. Toth and G. Lang: *J. Electrochem. Soc.*, 2000, **147**, 3311.
24. S. Yoon, M. Schnoartz and K. Nobe: *J. Electrochem. Soc.*, 1995, **82**, 64.
25. Y. Fukumoto: *J. Met. Fin. Soc. Japan*, 1989, **39**, 162.
26. K. Mosokawa: *J. Met. Fin. Soc. Japan*, 1988, **39**, 156.
27. J. R. White: *J. Appl. Electrochem.*, 1987, **17**, 977.
28. O. Chene and D. Landolt: *J. Appl. Electrochem.*, 1989, **19**, 188.
29. H. Eisazadeh, G. Spinks and G. G. Wallace: *Polym. Int.*, 1995, **37**, 87.
30. H. Eisazadeh, K. J. Gilmore, A. J. Hodgson, G. Spinks and G. G. Wallace: *Colloids Surf.*, 1995, (37103), 281.
31. N. Tabakova, N. Petkova and J. Stejskal: *J. Appl. Electrochem.*, 1998, **28**, 1083.
32. E. E. Farndon, F. C. Walsh and S. A. Campbell: *J. Appl. Electrochem.*, 1995, **25**, 574.
33. W. U. Schmidt, R. C. Alkire and A. A. Gewirth: *J. Electrochem. Soc.*, 1996, **143**, 3122.
34. R. C. Alkire and E. D. Eliadis: *Z. Phys. Chem.*, 1999, **208**, 1.
35. M. Sendo and J. Malyszko: *J. Electrochem. Soc.*, 1996, **147**, 1758.
36. H. Natter and R. Hempelmann: *J. Phys. Chem.*, 1996, **100**, 19525.
37. T. Pearson and J. K. Dennis: *Surf. Coat. Technol.*, 1990, **42**, 69-79.
38. T. Pearson and J. K. Dennis: *J. Appl. Electrochem.*, 1990, **20**, 196-208.