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# Electrochemically deposited Ni + WC composite coatings obtained under constant and pulsating current regimes

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## Abstract

A series of Ni + WC composite coatings were obtained by electrodeposition on a rotating disc electrode (RDE) from a commercially available Watts bath containing additives for brightness and smoothing and insoluble WC particles, using either constant or pulsating current. It was shown that the amount of WC embedded in the coating could vary from a few percent to over 80% depending on the rotation rate and the current density of deposition. Higher amounts (over 50 mass%) of embedded WC particles could be obtained only at rotation rates higher than 2000 rpm. It was also shown that the concentration of insoluble WC particles in the Watts bath has no significant influence on the amount of WC embedded in the coating, enabling the use of dilute mixtures (2 mass% of WC in the solution). At higher amounts of embedded WC particles, rough deposits were obtained with the WC particles being mostly incorporated in agglomerates of different sizes (from about 50 $\mu$m to about 100 $\mu$m). It was also shown that under the same conditions of electrodeposition, higher amounts of embedded WC particles could be obtained from solutions containing smaller particles.

## 1. Introduction

One type of electrodeposited composite coating consists of a base metal with embedded dispersed particles. These particles are insoluble in the electrolytes used for electrodeposition of the base metal and are mechanically dispersed to create a homogeneous medium [1–3]. The particles to be incorporated can be hard oxides or carbides such as: $Al_2O_3$, SiC, $TiO_2$, WC, $SiO_2$ [4]. These coatings are used in a wide variety of industries [5–8].

Nickel based electrochemical composite coatings have good corrosion properties and enhanced electrochemical activity for hydrogen and oxygen evolution compared to the base metal [9, 10]. These coatings are also used for the protection of machine parts subject to aggressive environments [11, 12]. To improve Ni based coatings, it is possible to incorporate pure metal particles, such as W, Ti, Al, Mo [13–20], or some oxide particles [4]. Such procedures lead to better catalytic activities, enhanced corrosion resistance, and increased hardness and thermal resistivity [21–24]. Based on the literature, [25–30] the Ni based composite coatings were first deposited from a slurry containing more than 10 mass% of insoluble particles. Slow transport of material to the surface of the working electrode was claimed to require a large concentration of WC in the bath [30]. Increase in the collision frequency of the particles with the electrode was found to increase the incorporation of particles into the coating [31, 32]. The collision frequency was increased by increasing the concentration of particles in the bath. However, with increasing concentration of particles in the electrolyte, collisions between the particles in the electrolyte, as well as collisions between the particles attached to the cathode and the particles in the electrolyte, are also intensified. Consequently, more collisions become inefficient and some of the particles incorporated into the coating during the initial period of deposition become detached from the cathode [31, 32]. Mass transfer of the insoluble particles towards the cathode also influences the deposition process. The slower the mass transfer, the higher the required concentration of particles in the electrolyte [31, 32]. Therefore, it is important to establish the optimum concentration of particles in the electrolyte for a given deposition regime and stirring conditions. The maximum amount of embedded WC in commercial Ni based coatings was found to be about 30% [25–30].

In this work an attempt was made to investigate the effects of concentration and the size of the WC particles, as well as the coating thickness, deposition current densities during constant and pulsating regimes and the electrode rotation rate on the properties and composition of Ni + WC electrodeposited composite coatings.

## 2. Experimental details

All experiments were carried out in a standard, three-electrode electrochemical cell. A RDE (Tacussel Controvit) with a changeable disc made of steel was used as the cathode, while Ni was used as the anode. A saturated calomel electrode (SCE), placed in a separate compartment and connected to the working electrode compartment by means of Luggin capillary, was used as the reference electrode.

The series of experiments was carried out in a commercial Ni-Watts bath containing 2, 20 and 30 mass% of WC (Voksal, Uzice) of 99.8% purity (less then 20 ppm of Al, Ni, Ca, Cr, Fe, Mo and Si). The average particle size was determined by the Fisher method. A magnetic stirrer was used for mixing the electrolyte to obtain a homogeneous medium before the experiments.

The samples were analyzed, as deposited, using SEM (JSM-533, JEOL) with an EDS system (ANALYTICAL Qx200). The composition of the coatings was analyzed at about 10 places on the metal surface of each sample at a magnification of 1000×.

Samples for cross-section examination were sealed in epoxy resin and cut. The cross-section was first polished with emery papers (120–4000 grades) and subsequently on polishing cloths impregnated with diamond paste (3, 1 and 0.3 $\mu$m grades), etched in aqua regia and then scanned with an optical device LEICA-Q500 MC. For qualitative measurements and analysis, Q-WIN software was used. A metallographic microscope linked with a LEICA-DC150 was used for photographing the samples.

A programmable potentiostat (PAR 273) was used for constant and pulsating current regimes of deposition.

## 3. Results and discussion

At the beginning of this study it was found that, under the same conditions of electrodeposition, the amount of WC in the electrolyte did not exhibit a significant influence on the amount of WC incorporated into the coating. The composite coatings obtained had approximately the same composition regardless of which of the three electrolytes, with a rather wide range of WC concentrations, varying from 2 mass% to 30 mass%, was used. The results are presented in Table 1. Hence, further experiments were carried out from a bath containing 2 mass% of WC which was adequately fluid compared to the slurries with higher WC concentrations.

*Table 1.* Dependence of the mass% of WC imbedded in a Ni deposit on the mass% of WC in the deposition solution: particle size 0.4 $\mu$m, constant current density $j = 5$ mA cm$^{-2}$, rpm = 3000

| Concentration of WC particles in the solution /mass% | Content of WC particles in the deposit /mass% |
|---|---|
| 2 | 80 |
| 20 | 78 |
| 30 | 83 |

Depending on plating conditions, coatings with a low content of WC (up to about 10 mass%) were bright, while those with higher amounts of WC (over about 50 mass%) were rough and were similar in appearance to emery paper.

### 3.1. *Influence of the calculated coating thickness formed using a constant current and constant rotating rate on the amount of WC embedded*

The apparent thickness of the deposit was obtained assuming that pure Ni deposition takes place with 100% current efficiency.

In all cases, it was found that the WC content shows some tendency to increase with increasing apparent coating thickness. This is shown in Figure 1 for a deposit obtained at a constant current density of 2.5 mA cm$^{-2}$ at rpm = 3000. The amount of WC embedded in the deposit increases faster with increasing thickness for thinner deposits (up to 2 $\mu$m), while for thick deposits the amount of incorporated WC particles approaches approximately 75 mass%. This behavior indicates that the process of incorporation of WC

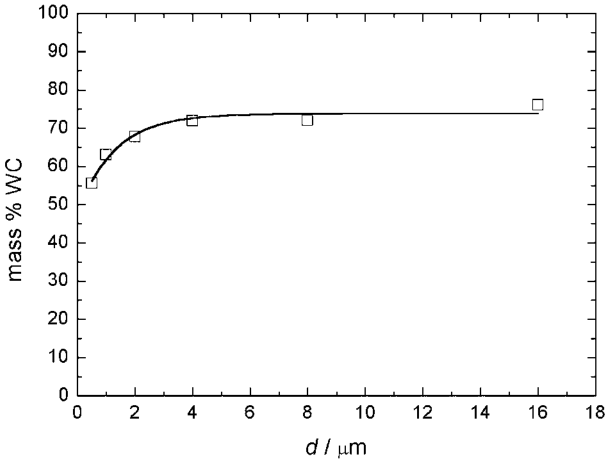

*Fig. 1.* Dependence of the mass% of embedded WC particles of size 0.4 $\mu$m in the Ni deposit as a function of the apparent deposit thickness, obtained at a current density of 2.5 mA cm$^{-2}$ and rpm = 3000.

particles is slower than that of Ni electrodeposition and that longer times are needed for higher amounts of WC to be embedded.

### 3.2. *Influence of deposition current density, rotating rate and particle size on the amount of WC embedded at constant current*

As can be seen in Figure 2, the amount of WC increases linearly with increasing current density (both with particle dimensions of 0.4 and 0.7 $\mu$m). The rotation rate is seen to have a profound influence on the WC content of the deposit. High WC contents can be obtained only at high rotation rates. It was found that under the same conditions of electrodeposition higher WC contents can be obtained with smaller particles.

It has been shown by calculation [33] that inert particles can reach the surface of a rotating disc electrode by internal forces alone only if the following condition is fulfilled

$$3.52\rho_p r_p^2 v^{-1}\omega < 0.75 \qquad (1)$$

where $\rho_p$ and $r_p$ are, respectively, the density and the radius of the inert particle. It was also shown (for the case of Cu electrodeposition with the inclusion of $Al_2O_3$ inert particles [34–36]) that laminar flow is established at rpm $\leqslant$ 350, that turbulent flow is established at rpm $\geqslant$ 1100, while a transition zone exists in between. Furthermore, it was shown that the content of inert particles in the deposit can increase in this transition zone and that such an increase is the consequence of the formation of inert particle agglomerates and their codeposition with the base metal. Applying this to our case, it can be concluded that particles of 0.4 and 0.7 $\mu$m can reach the electrode surface at rpm $\geqslant$ 250 and rpm $\geqslant$ 80, respectively. Hence, only a relatively low percentage of WC is expected to be embedded in Ni deposit at rpm = 1000. As can be seen in Figure 2, only when high values of current densities were used was a small percentage of WC observed in the deposit obtained at rpm = 1000 (for both sizes of WC particles). It appears that the deposition of the base metal (Ni) at high current densities is fast enough to occlude some of the particles and incorporate them into the deposit. It is interesting to note that at rpm = 2000 there was no significant difference in the amount of WC embedded in the deposit from electrolyte containing particles of different sizes. However, at rpm = 3000 there was a significant difference in the WC content at all applied current densities. The amount of WC was found to be approx. 20% higher in the deposit obtained from the electrolyte containing 0.4 $\mu$m particles compared to that containing 0.7 $\mu$m particles. This is reasonable in view of the fact that the time necessary for the adherence of smaller particles is shorter than that for larger particles, as well as that the amount of smaller particles reaching the electrode surface is higher.

### 3.3. *The influence of deposition current density, rotating rate and particle size on the amount of WC embedded with pulsating current*

The influence of pulsating current regime parameters on the composition of Ni + WC coatings are shown in Figures 3 and 4.

As can be seen in Figure 3, the content of WC in the deposit approaches a maximum at frequencies higher than 20 Hz for both particle sizes. As in the case of constant current, higher amounts of embedded WC were detected for the smaller 0.4 $\mu$m particles. The lower values of the WC content obtained at lower frequencies ($v$ < 20 Hz), may be explained by 'tearing off' of the particles and their reintroduction into solution during off periods of the current. At lower frequencies, the off

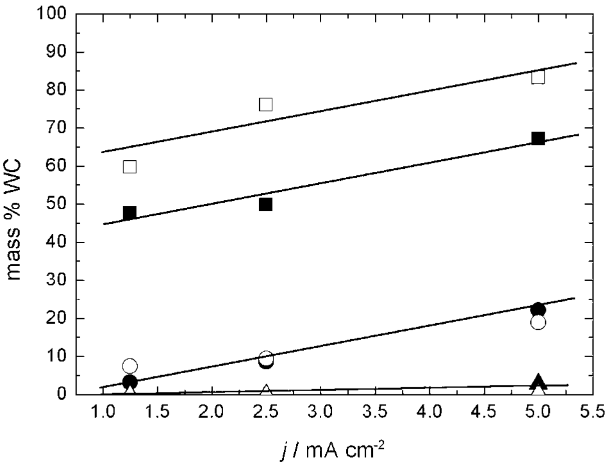

*Fig. 2.* Dependence of the mass% of embedded WC particles of size 0.4 $\mu$m (△,○,□) and of size 0.7 $\mu$m (▲,●,■) in the Ni deposit as a function of the constant current density at rotation rates of: (△,▲) 1000 rpm; (○,●) 2000 rpm; (□,■) 3000 rpm.

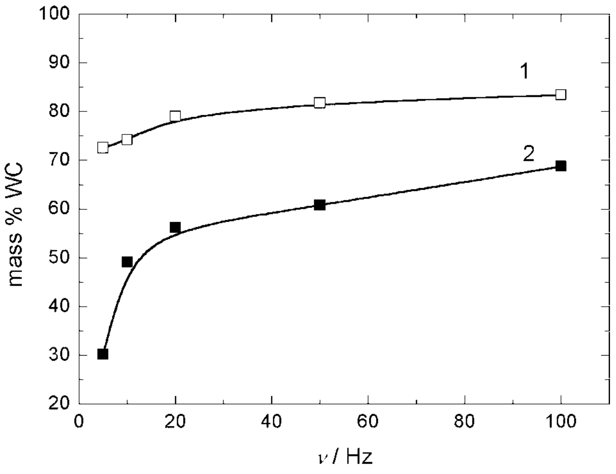

*Fig. 3.* Dependence of the mass% of embedded WC particles of size 0.4 $\mu$m (1), and of size 0.7 $\mu$m (2) in the Ni deposit as a function of the frequency ($v$) of the pulsating current, obtained at an average current density of 2.5 mA cm$^{-2}$ and rpm = 3000.

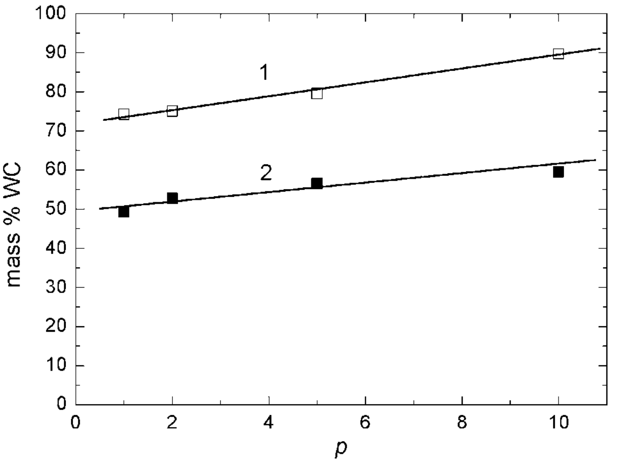

*Fig. 4.* Dependence of the mass% of embedded WC particles of size 0.4 $\mu$m (1), and of size 0.7 $\mu$m (2) in the Ni deposit as a function of the pause/pulse ratio ($p$) of the pulsating current, obtained at an average current density of 2.5 mA cm$^{-2}$ and rpm = 3000.

period is longer and, accordingly a higher number of particles are 'removed' from the electrode surface. This behavior is in accordance with the shape of these dependencies for smaller (1) and bigger (2) particles, i.e. a significantly sharper increase in the amount of WC particles is seen for the bigger particles indicating that the 'tearing off' of bigger particles is more sensitive to the length of the pulsation off period. In both cases the off time at frequencies higher than 20 Hz is too short to allow the 'tearing' effect to take place and the system behaves as in the case of constant current.

The dependence of the mass% of WC on the pause to pulse ratio, with a mean value of current density of 2.5 mA cm$^{-2}$ and a frequency of 10 Hz is shown in Figure 4. Linear dependencies were obtained for both particle sizes. In the given case, two different effects influence the WC content in the coating. The first is the increase in the current efficiency of Ni deposition with increasing current density during the pulse, since the average current density is defined as

$$j_{\mathrm{av}} = \frac{j_{\mathrm{c}} t_{\mathrm{c}}}{t_{\mathrm{c}} + t_{\mathrm{p}}} = \frac{j_{\mathrm{c}}}{1 + p} \tag{2}$$

with $j_{\mathrm{c}}$ being the current density of the pulse and $p$ the ratio between the pause ($t_{\mathrm{p}}$) and the pulse duration ($t_{\mathrm{c}}$), i.e. $p = t_{\mathrm{p}}/t_{\mathrm{c}}$ [37]. The consequence of this is a more efficient occlusion of WC particles with Ni during the pulse period. The second effect is that with increasing duration of the off period the 'tearing' effect of the particles from the surface becomes more pronounced. Those two phenomena have a counteracting effect. The results indicate that the first effect is predominant since the content of WC embedded in Ni slightly increases with increasing $p$, i.e. with increasing $j_{\mathrm{c}}$. Once again, the systematic difference between the results obtained with the 0.4 and 0.7 $\mu$m particles, indicates that the larger particles more easily succumb to the 'tearing off' effect.

### 3.4. *Morphology of the composite Ni + WC coatings*

The commercial, buffered electrolyte used for the deposition of Ni + WC contains additives for brightness and smoothing and is known as an electrolyte with good throwing power. A cross-section of a steel disc with a composite coating on it containing a high amount of WC is shown in Figure 5a. It can be seen that, in spite of the good throwing power, the deposit is not a compact one. Non-uniformly distributed agglomerates of different sizes are seen scattered over the surface, the distances between them being much smaller than the dimensions of the agglomerates. One isolated agglomerate, of complex shape, is shown in Figure 5b at higher magnification. Such behavior is in accordance with previously reported results [36]. It is also reasonable to expect the formation of bigger agglomerates at higher rotation rates with a high content of embedded WC particles in the Ni deposit.

Figure 6 represents a much higher magnification of the cross-section of the Ni + WC coating, taken from one of the agglomerates. As can be seen, the particles are relatively homogeneously distributed within the agglomerate.

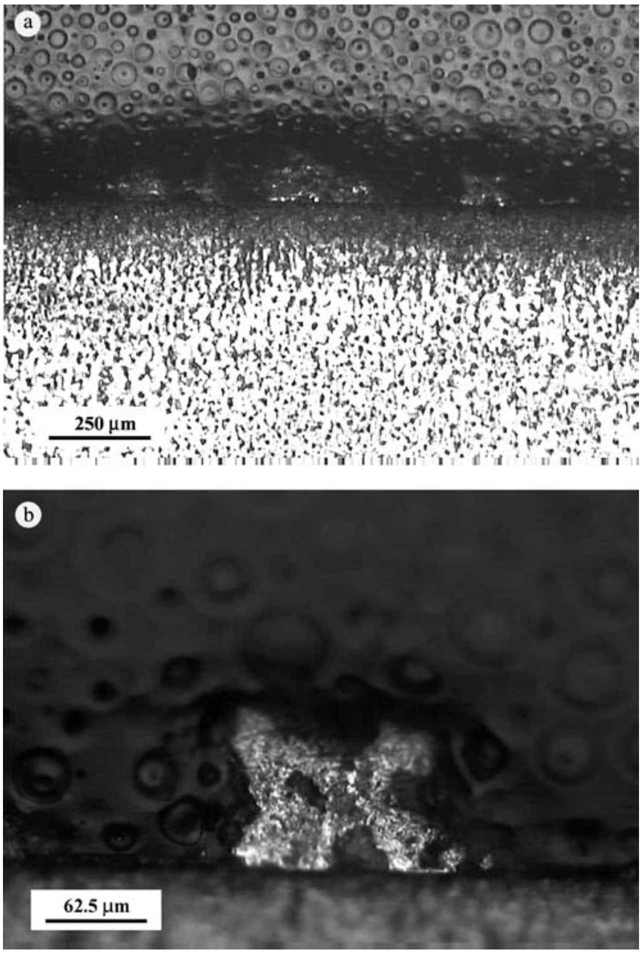

*Fig. 5.* (a) Cross-section of a Ni + WC composite coating with high content of WC (over 50 mass%) obtained by either constant or pulsating current at an average current density of 2.5 mA cm$^{-2}$ and rpm = 3000. (b) One isolated agglomerate.

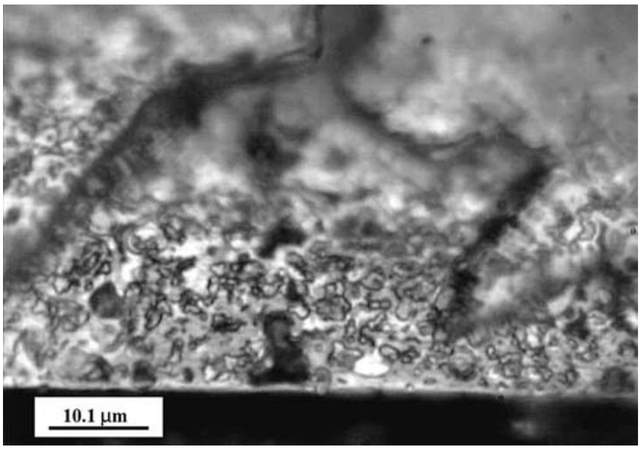

*Fig. 6.* High magnification of the cross-section of one agglomerate of a Ni + WC composite coating with high content of WC (over 50 mass%) obtained by either constant or pulsating current at an average current density of 2.5 mA cm$^{-2}$ and rpm = 3000.

## 4. Conclusion

It has been shown that the amount of WC embedded in Ni + WC composite coatings, electrodeposited under either a constant or pulsating current regime from a commercially available Watts bath containing additives for brightness and smoothing and insoluble WC particles, may vary from a few percents to over 80% depending on the rotation rate and deposition current density. Higher amounts (over 50 mass%) of embedded WC particles could be obtained only at rotation rates higher than 2000 rpm. When the amounts of embedded WC particles were higher, rough deposits were obtained with the WC particles being mostly incorporated in agglomerates of different sizes (from about 50 $\mu$m to about 100 $\mu$m). It was also shown that under the same electrodeposition conditions, a higher amount of embedded WC particles could be obtained from the solution containing smaller particles.

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## References

1. J.R. Roos, J.P. Celis, J. Fransaer and C. Buelens, *J. Met.* **42** (1990) 60.
2. J. Fransaer, J.P. Celis and J.R. Roos, *J. Electrochem. Soc.* **139** (1992) 413.
3. A. Hovestad and L.J.J. Janssen, *Rev. Appl. Electrochem.* **40** (1995) 519.
4. S. Alexandriodou, C. Kiparissides, J. Fransaer and J.P. Celis, *Surf. Coat. Technol.* **71** (1995) 267.
5. B. Abeles, in R. Wolfe (Ed.), 'Applied Solid State Science: Advances in Materials and Device Research' (Academic Press, New York, 1976), p. 1.
6. R.R. Oberle, M.R. Scanalon, R.C. Cammarata and P.C. Searson, *Appl. Phys. Lett.* **66** (1995) 19.
7. S.W. Banovic, K. Barmark and A.R. Marder, *J. Mater. Sci.* **34** (1999) 3203.
8. K. Barmak, S.W. Banovic, C.M. Petronis, D.F. Susan and A.R. Marder, *J. Microscopy* **185** (1997) 265.
9. S.V. Muchnick and Ya.F. Lynchak, *Poroshkovaya Metallurgya Ukrain SSR* **28** (1989) 2.
10. M. Naka, K. Hashimoto and T. Masumoto, *Phys. Chem. Metallurg.* **28** (1990) 2.
11. D. Gierlotka, E. Rowinski, A. Budniok and E. Lagawiek, *J. Appl. Electrochem.* **27** (1997) 1324.
12. D.W. Jepsen and M. Marcus, *Phys. Rev. Lett.* **13** (1998) 11.
13. A. Serek and A. Budniok, *Archiwum Nauki materialach* **20**(4) (1999) 259.
14. A. Gruszaka and A. Budniok, *Adv. Perform. Mater.* **6** (1999) 141.
15. I. Naploszek-Bilnik and A. Budniok, *Kompozyty* **2** (2002) 52.
16. M. Popczyk, A. Budniok, J. Cybo and G. Sluzalek, *Kompozyty* **2** (2002) 68.
17. A. Serek and A. Budniok, *Kompozyty* **2** (2002) 63.
18. A. Serek and A. Budniok, *Kompozyty* **2**(3) (2002) 58.
19. J. Niedbala, *Kompozyty* **2** (2002) 369.
20. D.F. Susan and A.R. Marder, *Acta Mater.* **49** (2001) 1153.
21. C.W. Yuen and H.W. Kui, *J Mater. Res.* **13** (1998) 11.
22. D.S.W. Dos Santos and P.E.V. De Miranola, *Int. J. Hydrogen Energy* **23** (1998) 11.
23. J. Niedbala, A. Budniok, D. Gierlotka and J. Surowka, *Thin Solid Films* **226** (1995) 113.
24. B. Losiewicz, A. Stepien, D. Gierlotka and A. Budniok, *Thin Solid Films* **349** (1999) 43.
25. I. Garcia, J. Fransaer and J.P. Celis, *Surf. Coat. Technol.* **148** (2001) 171.
26. J.P. Celis, J.R. Roos and C. Buelens, *J. Electrochem. Soc.* **134** (1987) 1402.
27. J.P. Celis and J.R. Roos, *J. Electrochem. Soc.* **124** (1977) 1508.
28. P.M. Vereecken, I. Shao and P.C. Searson, *J. Electrochem. Soc.* **147** (2000) 2572.
29. N. Guglielmi, *J. Electrochem. Soc.* **119** (1972) 1009.
30. R.S. Saifulin, in 'Kombinirovannye elektrokhimicheskie pokrytiya i materialy', M. Khimiya (1972), p. 168.
31. R.S. Saifulin, in 'Kombinirovannye pokrytiya i materialy', M. Khimiya (1977), p. 272.
32. A.J. Antropov and Yu.H. Lebedinskii, in 'Kombinirovannye elektrokhimicheskie pokrytiya i materialy', Tekhnika, Kiev (1972).
33. M. Van Camp, Engineering Thesis, K.U. Leuven (1976).
34. D.W. Snaith and P.D. Groves, *Trans. Inst. Met. Finish* **50** (1972) 95.
35. C. Buelens, J.P. Celis and J.R. Roos, *J. Appl. Electrochem.* **13** (1983) 541.
36. J.R. Roos, J.P. Celis, H. Kelchtermans, M. Van Camp and C. Buelens, in S. Hawayama (Ed.), 'Proceedings of the 10th World Congress of Metal Finishing', The Metal Finishing Society of Japan, Kyoto (1980), p. 203.
37. K.I. Popov and M.D. Maksimović, in B.E. Conway, J.O'M. Bockris and R.E. White (Eds), 'Modern Aspects of Electrochemistry', Vol. 19, Ch. 3, Plenum Press, New York (1989).