

THE INFLUENCE OF THE STRUCTURE OF THE NANOCOMPOSITE Ni-PTFE COATINGS ON THE CORROSION PROPERTIES

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Abstract. The nanocrystalline composite electrochemical coatings prepared with nickel matrix and PTFE particles were investigated. Nickel plating bath of low nickel(II) concentration (0.75M) with organic compounds and dispersed PTFE particles content was used for coatings electrodeposition. PTFE particles content was determined gravimetrically. The roughness of the nickel foils was evaluated using a TR 100 prod. Elcometr Instruments Ltd. profilograph. The microhardness of the deposited layers was measured using a Vickers' method at a load of 0.01 and 0.05 kG. The following dependencies were obtained: $R_s=0.056 Cp+0.002D_{111}$, $HV_{0.01}=25.65/D_{111}^{1/2}$. Siemens D500 X-ray diffractometer with CuK_{α} radiation was used to determine the preferred orientation, the dimension of nickel [111] crystallites and microstress. The size of [111] nickel crystallites in the Ni-PTFE coatings was from 11 to 39 nm. All coatings have the approximately random orientation. Decreasing of the crystallite size in the nickel coating influenced on the increase microstress. Voltammetric method was used for examination of the samples of composite coatings during tests in 0.5M NaCl, pH 7. Results were used for calculation of the free corrosion potential and current. The corrosion resistance of all of the composite coatings was superior to that of the nickel coating. Non-conducting PTFE particles incorporated into a nickel coating also occur on its surface, which should affect the corrosive behavior of the composite coating. The following dependence was obtained: $P=26.3P_{111}+1.5D_{111}$. The corrosion rate increase with increasing of the preferred orientation (111) content and with increasing of the dimension of nickel [111] crystallites.

1. INTRODUCTION

One of the basic reasons for electroplating coatings on parts of machines and structures is to improve the functional properties of products exposed to external hazards.

Electrodeposition can be used to produce composite coatings on a nickel matrix [1-3]. In comparison with conventional coarse-grained coatings, electroplated nanocrystalline nickel coatings are characterized by greater resistance, microhard-

ness, diffusion coefficient, electrical resistance, specific heat, coefficient of thermal expansion, plasticity, adhesion, corrosion- and wear resistance, as well as a lower elasticity modulus, exceptionally soft magnetic properties, and thermal stability up to a temperature of 573K [4].

Advances in electrodeposition of composite coatings [5] have opened up prospects for obtaining layers with exceptional properties. Producing a good composite layer, often with previously un-

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achievable properties, requires not only the proper choice of components, but also attaining the appropriate structure of the composite material. The structure and composition of electroplated coatings, including composite coatings, have a major influence on their physical and mechanical properties such as internal stress, roughness, gloss, microhardness, wear resistance, and corrosion resistance. Determining the relationship between a coating's structure and composition and the composition of the bath in which it was produced, makes it possible to select the parameters for depositing coatings with the best properties. Important considerations include not only the influence of particles in the process of electrocrystallization of coatings, but also the influence of organic compounds, which can modify the structure and properties of the metal matrix.

Self-lubricating coatings, such as Ni-PTFE, have been the subjects of recent publications [6,7]. PTFE particles are practically resistant to chemicals, do not absorb water, have a wide range of service temperatures (-190 to +260 °C) and have excellent wear and aging characteristics. They also have a very small friction coefficient, about 0.02, thanks to which they have excellent sliding properties and reduce adherence [8]. PTFE particles incorporated into a nickel coating increase wear resistance and reduce the friction coefficient in comparison with electroplated nickel without dispersion particles. It is also important for these coatings to have good corrosion resistance in aggressive environments such as 0.5 M NaCl.

An aqueous suspension of PTFE in a nickel electrolyte undergoes flocculation as the result of van der Waals forces. Modifying the composition of the bath to allow the particles to remain in suspension until they are incorporated into the coating can counteract this. Ramesh Babu *et al.* [9] reported on the effect of electrodeposition parameters in Watts electrolyte on the PTFE content in the obtained Ni-PTFE layers.

In the current study we examined the relationship between the structure of nanocrystalline coatings Ni-PTFE, their corrosion resistance, and other properties, such as those that may be important in wear resistance.

2. EXPERIMENTAL

To study the electrodeposition of nickel coatings, a low-concentration nickel-plating bath containing 0.45M NiSO₄·xH₂O, 0.3M NiCl₂·6H₂O, 0.85M H₃BO₃ was used. Additives, sodium o-benzosulfamide

(saccharin, SA) at a concentration of 15 mM, and butyne-2-diol-1,4 (BD) at a concentration of 5 mM, were included in the bath either singly or together. The dispersion particles used in the study were the polytetrafluoroethylene: PTFE particles -100 nm (DT 50% dispersion) from ZA Tarnów.

Electroplating process was realized at current density of 4 A/dm², at temperature of 318K and pH 4 during 1800 s. Stirring with a magnetic mixer at 100 rpm was employed. Dispersed phase content in the coating was determined gravimetrically. The roughness of the nickel foils was evaluated using a TR 100 prod. Eicometr Instruments Ltd. profilograph.

The microhardness of the deposited layers was measured using Vickers' method and a Hanneman microhardness tester at a load of 0.0981 N (0.01 kG) and 0.49 N (0.05 kG). X-ray diffractometer measurements of deposited layers were made using a Siemens D500 powder diffractometer equipped with a semiconductor Si[Li] detector. CuK_α radiation was used. The lamp parameters were: U=40 kV, I=30 mA. The measurements were taken incrementally, in the range of 2θ 10°-100° every 0.05° with a measurement time of 2 sec. A value of $P_{hkl} > 1$ points to a preference for positioning the given *hkl* planes parallel to the surface of the sample, and conversely, $P_{hkl} < 1$ points to a preference for nonparallel positioning of the given *hkl* planes to the surface of the sample. The structural parameters of Ni crystallites were determined by analysis of reflexes 111 and 222 (half-intensity width and position), which broadening is derived from the size crystallites and microstrain (fluctuation of the lattice constants) and may be this described by a Cauchy type curve.

Resistance to corrosion was determined by the voltammetric method in a three-electrode system. The reference electrode was a chloride-silver electrode, the auxiliary electrode, a platinum electrode. The working surface of the electrode subjected to corrosion was 1 cm². The tests were conducted at a temperature of 293±2K. The basic element of the measuring system was a computer-controlled Atlas 98 potentiostat from Sollich. The POL-99 computer program was used to steer, acquire and perform the graphic and quantitative analysis of data. The potential was changed at a rate of 1 mV/s. The experiment was conducted in a 0.5M solution of sodium chloride that was not deoxidized, pH 7. The $i=f(E)$ curves were registered in a range of ±0.3 V from the stationary potential. The obtained Tafel curves were used to calculate the corrosion cur-

rent and potential, and corrosion rate. The percentage reduction of the corrosion rate P is defined as:

$$P = \frac{r_{\text{corr}} - r_{\text{corr},i}}{r_{\text{corr}}} 100\%, \quad (1)$$

where r_{corr} and $r_{\text{corr},i}$ denote the corrosion rate the same of a material produced with or without the presence of an inhibitor.

3. RESULTS

Table 1 presents the particle contents in composite Ni-PTFE coatings, corrosion current densities, corrosion potentials, corrosion rates, microhardness, and roughness of the coatings. The polar densities, average dimensions of nickel [111] crystallites and microstrains in Ni-PTFE coatings are presented in Table 2. Fig. 1 shows dependence of the corrosion current in 0.5 M NaCl on the content of PTFE particles in the composite layer. Fig. 2 shows dependence of the percentage reduction of the corrosion rate on nickel [111] crystallite size and polar density (111). Fig. 3 shows dependence of the percentage reduction of the corrosion rate on the PTFE particle content in a composite coating.

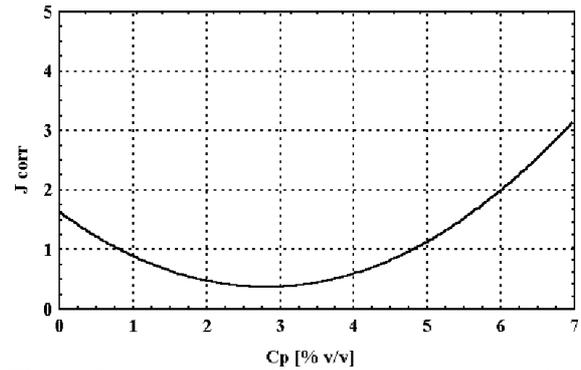


Fig. 1. Dependence of the corrosion current density in 0.5M NaCl on the content of PTFE particles in the composite layer.

4. DISCUSSION

The structure of composite coatings can be modified not only by incorporating dispersion particles, but also by adding organic compounds to the nickel bath. The latter approach was used in this study.

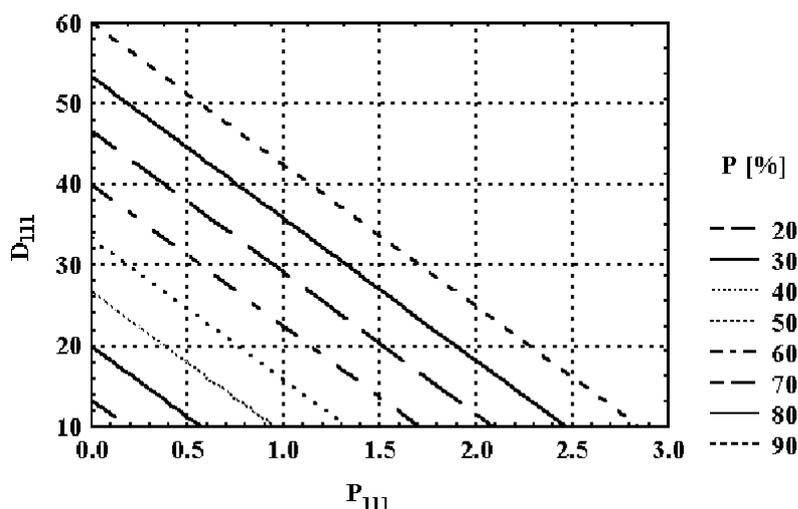
Increasing the content of PTFE particles in the bath increased their content in the deposited composite layers (Table 1). The organic compounds

Table 1. The particle contents in composite Ni-PTFE coatings, corrosion current densities, corrosion potentials, corrosion rates, microhardness, and roughness of the coatings.

Additives	C_p	J_{corr}	E_{corr}	r_i	HV	HV	R_a
	% v/v	$\mu\text{A}/\text{cm}^2$	mV	mm/year	[GPa]	[GPa]	μm
Without	0	1.71	-221	0.02103	2.60	2.0	0.27
15 g/dm ³ PTFE	4.13	0.427	-160	0.00525	3.38	3.03	0.38
15 g/dm ³ PTFE +15 mM SA	3.39	0.646	-185	0.00794	7.29	5.85	0.23
15 g/dm ³ PTFE + 5 mM BD	1.64	1.413	-270	0.01737	5.41	4.34	0.10
15 g/dm ³ PTFE + 15 mM SA + 5 mMBD	1.43	0.427	-222	0.00525	7.68	5.98	0.13
30 g/dm ³ PTFE	5.33	0.447	-108	0.00549	3.94	3.27	0.26
30 g/dm ³ PTFE + 15 mM SA	1.15	0.794	-218	0.00977	6.39	5.85	0.24
30 g/dm ³ PTFE + 5 mM BD	2.91	0.269	-175	0.00331	4.63	3.97	0.21
30 g/dm ³ PTFE + 15 mM SA + 5 mMBD	0.74	0.468	-226	0.00575	7.48	5.85	0.24
45 g/dm ³ PTFE	6.49	3.162	-265	0.03888	3.04	2.70	0.37
45 g/dm ³ PTFE + 15 mM SA	2.84	0.891	-240	0.01096	8.23	5.99	0.37
45 g/dm ³ PTFE + 5 mM BD	4.01	0.631	-200	0.00776	4.54	3.90	0.30
45 g/dm ³ PTFE + 15 mM SA + 5 mMBD	1.64	0.598	-230	0.00736	7.29	5.98	0.27

Table 2. The polar densities, average dimensions of nickel [111] crystallites and microstrains in Ni-PTFE coatings.

Additives	Polar density P_{hkl}				D_{111} [nm]	$\Delta a/a$
	[111]	[200]	[220]	[311]		
Without	0.950	0.599	0.113	2.339	38.0	0.0000
15 g/dm ³ PTFE	0.265	6.83	0.089	0.243	34.6	0.0002
15 g/dm ³ PTFE + 15 mM SA	0.831	0.828	1.617	0.791	11.2	0.0014
15 g/dm ³ PTFE + 5 mM BD	0.864	0.878	1.183	0.984	29.8	0.0023
15 g/dm ³ PTFE + 15 mM SA+5mMBD	2.278	1.029	0.326	0.904	15.1	0.0028
30 g/dm ³ PTFE	0.287	6.891	0.074	0.228	38.9	0.0022
30 g/dm ³ PTFE + 15 mM SA	1.041	0.928	1.320	0.845	12.5	0.0019
30 g/dm ³ PTFE + 5 mM BD	0.913	1.107	0.966	1.019	30.8	0.0021
30 g/dm ³ PTFE + 15 mM SA+5mMBD	1.903	1.207	0.490	0.902	14.0	0.0044
45 g/dm ³ PTFE	0.245	7.34	0.045	0.144	39.5	0.0015
45 g/dm ³ PTFE + 15 mM SA	1.042	0.825	1.484	0.788	12.7	0.0024
45 g/dm ³ PTFE + 5 mM BD	0.932	1.375	0.891	0.984	30.6	0.0022
45 g/dm ³ PTFE+15 mM SA+5 mM BD	1.433	1.064	0.866	0.907	11.0	0.0011

**Fig. 2.** Dependence of the percentage reduction of the corrosion rate on nickel [111] crystallite size and polar density (111).

used in the study inhibited the incorporation of PTFE into the nickel matrix to varied degrees. The least PTFE was incorporated from baths containing SA, BD, and 30 g/dm³ PTFE.

The size of the nickel [111] crystallites varied in all of the composite coatings and ranged from 11 to 40 nm (Table 2). The size of the nickel [111] crystallite deposited from the low-concentration bath was ~38 nm. The PTFE particles incorporated into the composite coating did not restrict the growth of

nickel grains, as their dimensions were similar to those in the nickel coating. The addition of BD to the nickel bath slightly decreased the growth of nickel [111] crystallites. The greatest effect was seen with saccharin, also when added together with BD, as the use of these additives together in the bath reduced the size of the nickel crystallites even to 11 nm (Table 2).

The nickel coating had a (311) texture, so the strong (100) texture exhibited by all of the com-

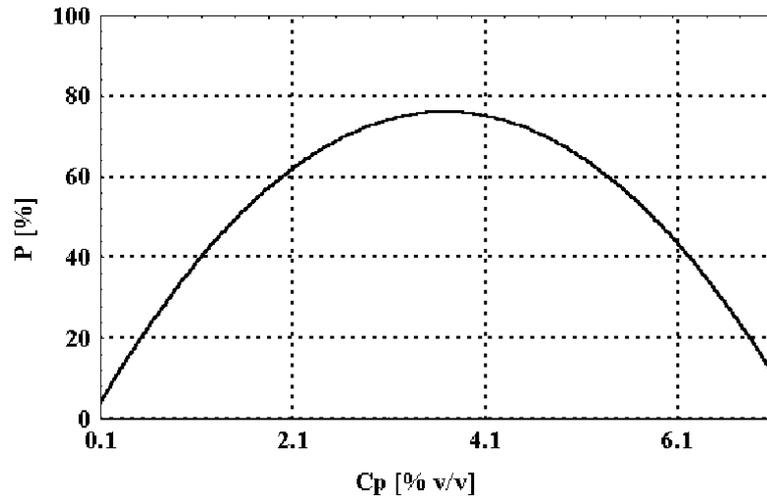


Fig. 3. Dependence of the percentage reduction of the corrosion rate on the PTFE particle content in a composite coating.

posite coatings deposited from baths without additives indicated that the dispersion particles reduced the rate of the electrode reaction. According to Reddy's theory [10], also defined with Wilman [11], the ratio of the mass transport rate to the ion reduction rate on the cathode reflects macroscopic growth. When the mass transport rate is greater than the ion reduction rate, the low-index planes will grow parallel to the substrate surface. Conversely, when the ion reduction rate exceeds the mass transport rate, the more slowly growing planes will be formed perpendicularly to the substrate surface. In Ni-PTFE coatings deposited without additives, low index (100) planes were formed parallel to the substrate surface. A completely different result was obtained for Ni-PTFE coatings deposited in the presence of saccharin, as they had a weak texture (110) as well as a large share of other orientations (Table 2). Acceleration of the development of this orientation and the greater resemblance of the orientation of Ni-PTFE coatings deposited, in the presence of saccharin, to a random orientation, may indicate, that all of the components of the bath from which the coating was deposited acted in such a way, that the growth rate in all crystallographic directions was more or less equal. The orientation of all of the Ni-PTFE coatings deposited in the presence of butindiol was close randomized (Table 2). When both additives were used together in a bath they slowed the growth rate of planes (110), and the deposited layers had a mixed (111)+(100) texture with a variable share

of orientation (111) as the concentration of PTFE particles in the bath increased. It was shown that by using organic compounds, randomized Ni-PTFE coatings with very small nickel [111] crystallites could be deposited, while reducing the amount of incorporated PTFE particles (Table 2). The effect of organic compounds on the structure of composite coatings is significant, and enables the production of layers with diverse physicochemical properties such as roughness, microhardness, or corrosion resistance.

The roughness R_a of the deposited Ni-PTFE coatings depended on the amount of incorporated particles C_p and also on the size of the nickel [111] crystallites D_{111} and was expressed as:

$$R_a = 0.056 C_p + 0.002 D_{111} \quad (2)$$

for $R=0.92$, where R is the correlation coefficient.

Increasing the content of PTFE particles in the composite layer and increasing the size of nickel [111] crystallites increased the roughness of the deposited layers. The use of organic compounds in baths enables depositing smoother Ni-PTFE coatings than obtained without these additives.

The microhardness $HV_{0.01}$ of the Ni-PTFE coatings depended on the size of nickel [111] crystallites, in keeping with the law of Hall - Fetch:

$$HV_{0.01} = \frac{25.65}{\sqrt{D}}, \quad (3)$$

for $R=0.99$

Saccharin, also together with butindiol, added to the bath produced Ni-PTFE layers with very small [111] crystallites, and therefore, greater microhardness. The dependence of the corrosion current density J_{corr} on the content of PTFE particles C_p in the coating was expressed as:

$$J_{corr} = 0.16C_p^2 - 0.9C_p + 1.64. \quad (4)$$

for $R=0.8$

Increasing the content of PTFE particles incorporated into the composite layer reduced the corrosion current density J_{corr} to minimal values, but only up to a PTFE content of 2.8% v/v. Above this value, the corrosion current increased (Fig. 1). Fig. 1 shows that increasing the content of incorporated PTFE particles to more than 5.5% v/v is unproductive, since this leads to lowering the corrosion resistance of the layer.

The structure of the deposited Ni-PTFE coatings influenced the percentage decrease of the corrosion rates P of these coatings in 0.5M NaCl in comparison with a nickel coating. This dependence can be presented as:

$$P = 26.3P_{111} + 1.5D_{111} \quad (5)$$

for $R=0.96$.

As can be seen from Fig. 2, a reduction of over 90% in the corrosion rate of a composite coating in comparison with a nickel coating can be obtained by depositing Ni-PTFE coatings in the range of:

$$P_{111} > 3; D_{111} > 10 \text{ nm and } P_{111} = 0; D_{111} > 60 \text{ nm.}$$

An additional condition is, however, the content of the PTFE particles in the composite coating (Fig. 3). This relationship can be described with the following nonlinear regression equation:

$$P = -5.6C_p^2 + 41.3C_p \quad (6)$$

for $R=0.94$.

5. CONCLUSIONS

1. The appropriate bath composition was used to deposit composite Ni-PTFE coatings with a varied content of incorporated PTFE particles; a nanostructure, with nickel [111] crystallites even 10 nm in size and a varied or randomized texture.
2. The presented relationships support the conclusion that the content of dispersion particles in

composite coatings and the structure of these coatings significantly affect their roughness, microhardness and resistance to electrochemical corrosion.

3. An increase in the content of incorporated PTFE particles caused increased roughness of Ni-PTFE coatings and decreased corrosion current density as the PTFE particle content in the coating increased to 2.8% v/v, after which the corrosion current increased as the PTFE particle content in the coating increased.
4. Decreasing the size of the nickel [111] crystallites reduced the roughness of Ni-PTFE coatings, increased the microhardness of these coatings and decreased corrosion resistance in 0.5M NaCl.
5. An increase in the (111) orientation in the deposited Ni-PTFE coatings increased the corrosion rate of these coatings.
6. The presented relationships make it possible to select a bath composition for depositing Ni-PTFE coatings with the desired properties for a given application.

REFERENCES

- [1] B. Szeptycka and A. Gajewska // *Inzynieria Materialowa* **130** (2002) 453.
- [2] B. Szeptycka // *Kompozyty* **4** (2002) 248.
- [3] B. Szeptycka and A. Skrzyniowski, In: *Tagungsband zum 5 Werkstofftechnischen Kolloquium in Chemnitz* (2002), p. 20.
- [4] N.V. Myung, M. Schwartz and K. Nobe // *Plat. And Surf. Finish.* **87** (2000) 76.
- [5] L. Benea, P.L. Bonora, A. Borello, S. Martelli, P. Wenger, P. Ponthiaux and J. Galland // *J. Electrochem. Soc.* **148** (2001) C461.
- [6] N.M. Teterina and G.V. Khaldeev // *Zascita Metallov* **28** (1992) 473, in Russian.
- [7] A.R. Poeton // *Metals and Materials* (1988) 702.
- [8] K. Helle and F. Walsh // *Trans. Inst. Metal Finish.* **75** (1997) 53.
- [9] G.N.K. Ramesh Bapu and S. Mohan // *Plating and Surf. Finish.* **4** (1995) 86.
- [10] A.K. Reddy // *J. Electroanal. Chem* **6** (1963) 141.
- [11] A.K. Reddy and H. Wilman // *Trans. Inst. Metal Finish.* **36** (1959) 87.