

M. NOWAK\*, M. OPYRCHAŁ\*, S. BOCZKAŁ\*, J. ŻELECHOWSKI\*, A. NAJDER\*, M. KARASŃ\*

## EFFECT OF CATHODIC CURRENT DENSITY ON MICROSTRUCTURE AND PROPERTIES OF NICKEL COMPOSITE COATINGS

### WPLYW KATODOWEJ GĘSTOŚCI PRĄDU NA MIKROSTRUKTURĘ I WŁAŚCIWOŚCI NIKLOWYCH POWŁOK KOMPOZYTYWYCH

Studies were carried out to characterise the nickel composite coatings deposited on a 2xxx series aluminium alloy. The composite coatings were prepared in a Watts bath with the addition of fine-dispersed particles of  $\text{Al}_2\text{O}_3$  powder introduced in an amount of 100 g/l using current densities of 2, 4, 6 and 8 A/dm<sup>2</sup>. The morphology, structure, thickness and microhardness of the obtained composite coatings were described. The volume fraction of  $\text{Al}_2\text{O}_3$  particles in composite coating was determined. The corrosion resistance of thus produced coatings was examined. Based on the results of the conducted studies it was stated that all the produced coatings were characterised by good adhesion to the substrate, but coatings produced at high current densities were characterised by a lower content of the  $\text{Al}_2\text{O}_3$  reinforcing phase present in the composite.

*Keywords:* electrodeposition, current density, composite coatings,  $\text{Al}_2\text{O}_3$

W pracy przedstawiono badania charakteryzujące kompozytowe powłoki niklowe osadzone na stopie aluminium serii 2xxx. Powłoki kompozytowe wytwarzano w kąpeli Wattsa z dodatkiem drobnodispersyjnych cząstek proszku  $\text{Al}_2\text{O}_3$  w ilości 100 g/l przy zastosowaniu gęstości prądu: 2, 4, 6 oraz 8 A/dm<sup>2</sup>. Przedstawiono morfologię, strukturę, grubość oraz mikrotwardość uzyskanych powłok kompozytowych. Określono objętościowy udział cząstek  $\text{Al}_2\text{O}_3$  w powłoce kompozytowej. Zbadano odporność korozyjną wytworzonych powłok. Na podstawie przeprowadzonych badań stwierdzono, iż wszystkie uzyskane powłoki są dobrze przyczepne do podłoża, jednak powłoki uzyskane przy wyższych gęstościach prądów charakteryzują się niższą zawartością fazy zbrojącej  $\text{Al}_2\text{O}_3$  w kompozycie.

#### 1. Introduction

Electroplated nickel coatings are widely used in various industries. Attractive design, high corrosion resistance and favourable mechanical properties allow the use of such coatings for decorative, protective and technological purposes. Still better properties can be obtained, when composite coatings are produced. Composites are materials with new properties; they differ from the homogeneous and single-phase materials in that they are composed of at least two components, the properties of which are either better or new as compared to the individual components applied separately. In the case of nickel coatings, the reinforcing phase is often made of  $\text{Al}_2\text{O}_3$  particles [1,2]. The size and the amount of the introduced reinforcing phase determines the properties of the newly produced nickel composite coatings. Producing a composite layer of the hitherto unattainable properties is a process that consists not only in the selection of the optimum components of the layer, but also in producing a specific structure in the composite material.

One of the primary purposes of producing nickel composite coatings on parts of machines and equipment is to improve their performance properties. With the ever increasing needs of industrial practice, traditional coating materials are

no longer sufficient, hence the rapid development of various types of composite materials.

For the production of nickel composite coatings, baths of different chemical compositions are used. The most widely used in industry are Watts type baths, based on the three main components: nickel sulphate, nickel chloride and boric acid; amide sulphonate baths are quite popular, too. Studies were also conducted to obtain amorphous Ni-W layers from water solutions [3]. The thickness of the nickel coatings deposited on aluminium and its alloys is 3 to 40  $\mu\text{m}$ ; the thickness of technical coatings exceeds 50  $\mu\text{m}$ .

#### 2. Experimental

The nickel composite coatings were produced in a Watts bath of the following chemical composition:  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  250 g/l,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  30 g/l,  $\text{H}_3\text{BO}_3$  30 g/l with the addition of saccharin in an amount of 2 g/l. As hard dispersion particles embedded in the coating, aluminium oxide  $\text{Al}_2\text{O}_3$  with an average particle size of about 0.8  $\mu\text{m}$  was used in an amount of 100 g/l. Coatings were produced on the AlCu4MgSi (2xxx) aluminium alloy with zinc sublayer. To produce nickel composite coatings, the following parameters were applied:

\* INSTITUTE OF NON-FERROUS METALS IN GLIWICE, LIGHT METALS DIVISION IN SKAWINA, 19 PILSUDSKIEGO STR., 32-050 SKAWINA, POLAND

cathodic current density of 2-8 A/dm<sup>2</sup>, bath temperature of 60°C, pH 4, the coating time of 60 minutes. The bath was stirred with a magnetic stirrer 500 rpm using also a peristaltic pump (350 ml/min.). The composite coating microstructure was examined under a Philips XL30 scanning electron microscope (SEM). Coating thickness was measured on the specimen transverse section as observed under an OLYMPUS GX71 light microscope. The structure of alumina was examined with a D8 Advance X-ray diffractometer. The particle content in the composite coating was determined by computer image analysis. Microhardness of coatings was measured with a Buehler Micromet 5103 microhardness tester. The Zeta potential measurement was performed with a Malvern ZetaSizer Nano ZS. The abrasion test was carried out on samples with dimensions of 100×100 mm using a Taber Abraser Model 5155 tester, CS-17 abrasive wheels, a load of 1000 g and 500 abrasive cycles. The abrasion resistance test was performed after 24 h samples acclimation under the following environmental conditions: temperature 23±2°C, relative humidity 50±5%. Corrosion tests were performed on an AUTOLAB PGSTAT device Model 302. The working electrode was nickel-coated electrode with an area of 1.8 cm<sup>2</sup>. The reference electrode was Ag/AgCl/3M KCl electrode, and the auxiliary electrode was made of platinum. Polarisation measurements were performed in a glass electrolyser at 25°C using 1M NaCl as a corrosive solution. The polarisation rate was 5 mV/s.

### 3. Results and discussion

Microscopic observations were carried out (respective photographs are not shown in this article) and phase composition of the alumina powder was identified. Figure 1 shows the X-ray diffraction pattern of Al<sub>2</sub>O<sub>3</sub> powder used as a reinforcing phase in nickel composite coating. As a result of microscopic observations of Al<sub>2</sub>O<sub>3</sub> particles it was established that the size of these particles was below 1 μm, while the X-ray analysis results indicated that it consisted of crystallographically pure corundum powder. During the deposition of nickel coatings, based on the measurement of zeta potential, it was found that Al<sub>2</sub>O<sub>3</sub> dispersion in the nickel bath was very unstable (the measured potential was about -4 mV) and rapid sedimentation of particles was observed to take place as soon as mixing of the galvanising bath had ceased. Examining photographs of the transverse sections of composite coating samples it has been found that the particles tend to form larger clusters-agglomerates. The phenomenon of the formation of agglomerates of Al<sub>2</sub>O<sub>3</sub> in the coating was also mentioned by other authors [4-6].

The effect of cathodic current density on the percent content of Al<sub>2</sub>O<sub>3</sub> in composite coating is shown in Figure 2. From the conducted investigations it follows that for the examined system of Ni-Al<sub>2</sub>O<sub>3</sub>, at the cathodic current density equal to 4 dm<sup>2</sup>, a maximum content of the dispersion phase embedded in the coating is observed. A similar effect has been obtained by Saha et al. [7]. The cathodic current density is, along with the concentration of dispersion particulate, the parameter that affects in a most important way the percent content of particles dispersed in the electrolyte. Yet, based on the examined literature data, it is difficult to assess the real impact of this

parameter, since the experimental results provided by various researchers show a disparity too large. In the systems of Ni-Al<sub>2</sub>O<sub>3</sub> and Ni-SiC, the increasing cathodic current density resulted in a decrease of the percent content of particles dispersed in the composite. This was due to the fact that the process was running in a diffusion area, which means that the speed of the process was controlled by the transport of Ni<sup>2+</sup> ions to the cathode surface.

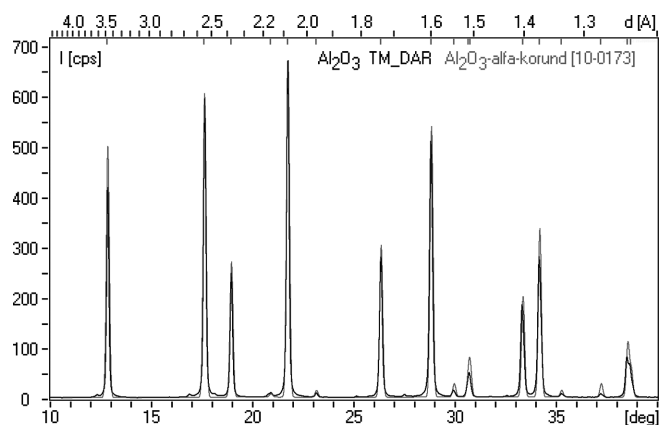


Fig. 1. X-ray diffraction pattern of Al<sub>2</sub>O<sub>3</sub> powder compared with the X-ray diffraction pattern of corundum  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

On the other hand, in the Ni-SiC system according to [8], the increasing cathodic current density increased the percent content of particles dispersed in the composite. This time, the reason was the fact that the process was running in an activation area, and the slow step was the reaction of transition.

Figures 4-7 show SEM images of microstructures examined on the transverse sections of produced coatings, while Figures 8-11 show microstructures on the transverse sections of coatings observed under an optical microscope. SEM observations show different distributions of Al<sub>2</sub>O<sub>3</sub>, depending on the current density applied. The Al<sub>2</sub>O<sub>3</sub> particles are fairly evenly distributed throughout the whole volume of the composite coating and are fully embedded in the metallic nickel matrix.

The effect of cathodic current density on the thickness of the obtained nickel composite coatings is shown in Figure 3. The thickness of coatings produced at a current density of 2A/dm<sup>2</sup> is 21.9 μm and it gradually raises to 75.8 μm for the current density value of 8 dm<sup>2</sup>.

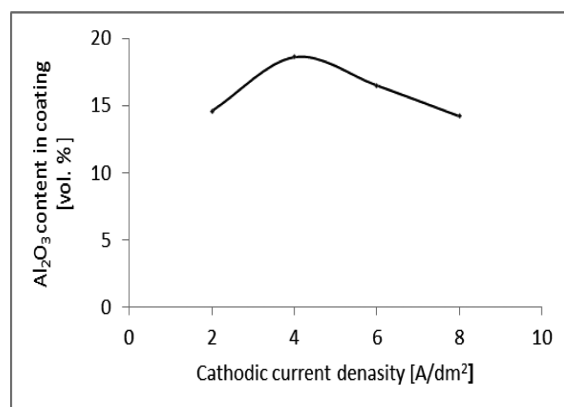


Fig. 2. Effect of cathodic current density on percent content of Al<sub>2</sub>O<sub>3</sub> particles in composite coating

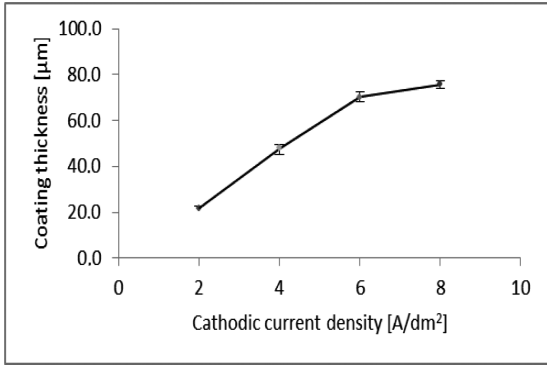


Fig. 3. Nickel coating thickness vs current density applied

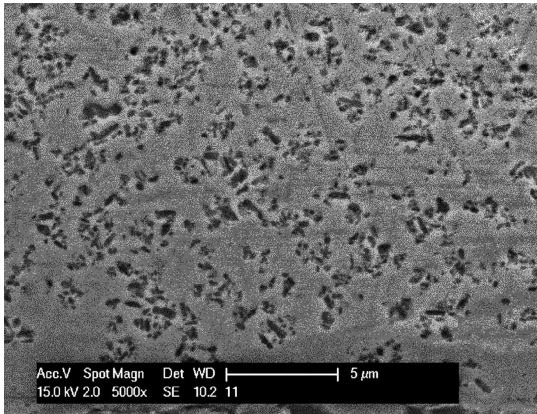


Fig. 4. Microstructure of coating produced at a current density of 2 A/dm<sup>2</sup>

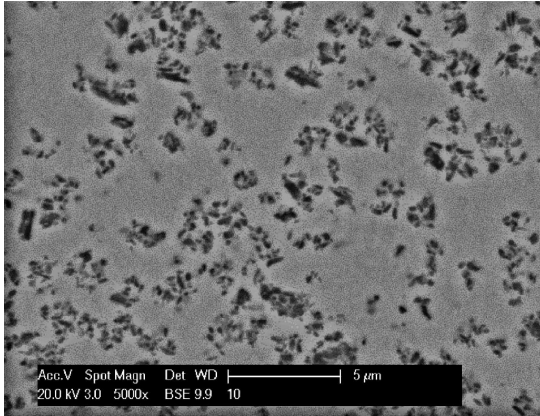


Fig. 5. Microstructure of coating produced at a current density of 4 A/dm<sup>2</sup>

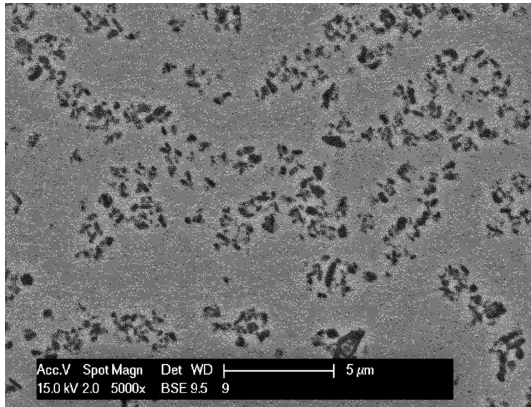


Fig. 6. Microstructure of coating produced at a current density of 6 A/dm<sup>2</sup>

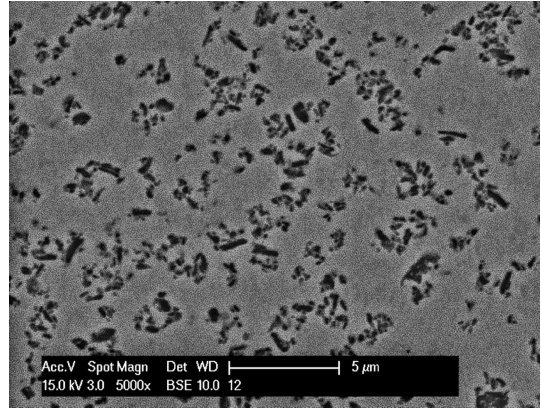


Fig. 7. Microstructure of coating produced at a current density of 8 A/dm<sup>2</sup>

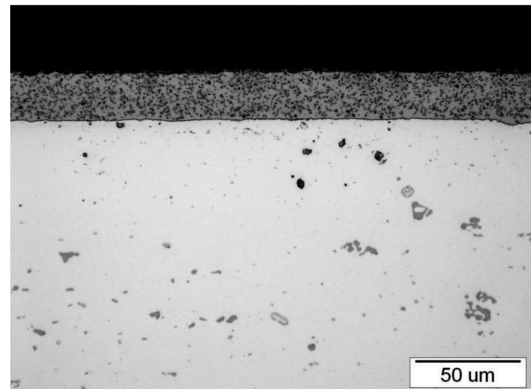


Fig. 8. Microstructure on the cross-section of coating produced at a current density of 2 A/dm<sup>2</sup>

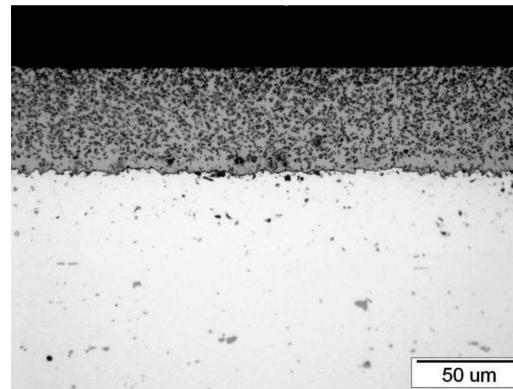


Fig. 9. Microstructure on the cross-section of coating produced at a current density of 4 A/dm<sup>2</sup>

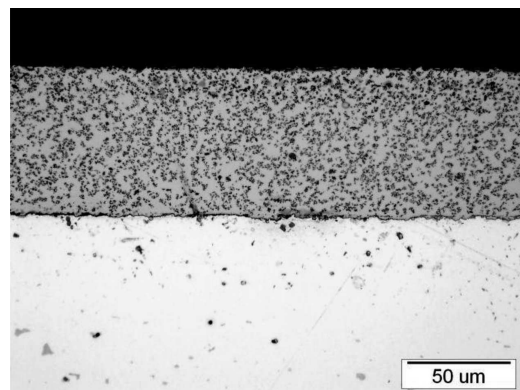


Fig. 10. Microstructure on the cross-section of coating produced at a current density of 6 A/dm<sup>2</sup>



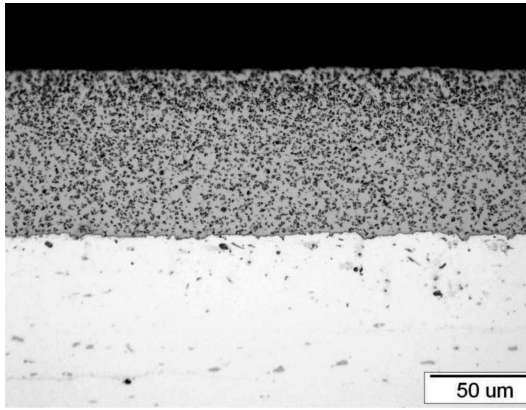


Fig. 11. Microstructure on the cross-section of coating produced at a current density of 8 A/dm<sup>2</sup>

The result of the abrasion wear resistance test is expressed as a coefficient of the wear of coating TWI (Taber Wear Index) calculated from equation (1):

$$TWI = \frac{W_b - W_a}{N} \times 1000 \quad (1)$$

where:

$W_b$  – weight of the sample before the test in mg,  $W_a$  – weight of the sample after the test in mg,  $N$  – number of cycles. A lower value of TWI indicates higher abrasion wear resistance. Based on the results obtained it was concluded that the best abrasion wear resistance could offer the coating produced at a cathodic current density of 4 A/dm<sup>2</sup>. The value of TWI for this coating was 31.4. The microhardness HV 0.01 of composite coatings measured on metallographic sections is shown in Table 1. From the results obtained it follows that the applied current density had no significant effect on the microhardness of coatings produced with the current density kept in a range of 2-6 A/dm<sup>2</sup>. Microhardness slightly increased and reached the value of about 482 HV 0.01 at a current density of 8 dm<sup>2</sup>. The coating microhardness increasing with the increasing cathodic current density was also observed by Xang Jin-Kang et al. [9]. Literature data also show the effect of cathodic current density on the size of the nickel crystallites formed during the process of electrodeposition. The increase in current density was accompanied by a decrease in the size of the crystallites formed [10, 11].

TABLE 1

Microhardness HV 0,01 of composite coatings measured on metallographic sections (Al<sub>2</sub>O<sub>3</sub> content 100 g/l)

Current density applied [A/dm <sup>2</sup> ]	HV 0,01
2	461.4
4	468.6
6	457.1
8	482.3

TABLE 2

The results of Taber abrasion resistance test (TWI) (Al<sub>2</sub>O<sub>3</sub> content 100 g/l)

Current density applied [A/dm <sup>2</sup> ]	TWI
2	41.2
4	31.4
6	35.6
8	36.6

The graph in Figure 12 and Table 3 show the results of electrochemical corrosion tests performed by potentiodynamic technique in 1 M NaCl solution. The potentiodynamic method is an electrochemical method during which the potential of the electrode changes continuously at a predetermined speed. Corrosion tests were carried out on samples immersed in naturally aerated 1M NaCl solution. The polarisation was initiated in 600 seconds after determining the, so-called, open-circuit potential. The polarisation curves obtained were plotted in a logarithmic scale. Respective values were used to calculate the corrosion potential –  $E_{corr}$ , the corrosion current –  $I_{corr}$  and the polarisation resistance –  $R_p$ .

The corrosion potential of the obtained composite coatings varies with the applied current density. The coating of the most cathodic character and the lowest corrosion was obtained with the current density value of 2 dm<sup>2</sup>. The values of the polarisation resistance proving the material resistance to corrosion are similar to each other, but the results obtained are higher compared to the values obtained by the authors in other studies using solutions without the addition of saccharin [12].

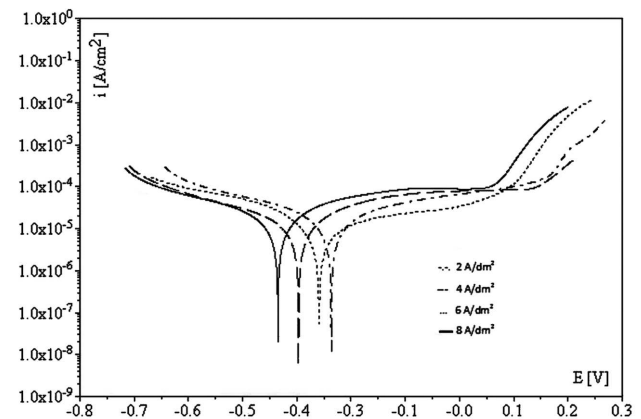


Fig. 12. Polarisation curves for the composite coatings produced at different cathodic current densities

TABLE 3

The results of potentiodynamic tests made in 1M NaCl solution

Results of electrochemical tests	Cathodic current density [A/dm <sup>2</sup> ]			
	2	4	6	8
$I_{corr}$ [A/dm <sup>2</sup> ]	$9.31 \cdot 10^{-6}$	$5.91 \cdot 10^{-6}$	$4.88 \cdot 10^{-6}$	$1.00 \cdot 10^{-5}$
$E_{corr}$ [mV]	-290	-356	-315	-398
$R_p$ [Ω]	$3.44 \cdot 10^3$	$2.27 \cdot 10^3$	$3.71 \cdot 10^3$	$2.51 \cdot 10^3$

#### 4. Conclusions

Coatings produced in a high concentration bath in the examined current density range of 2-8 dm<sup>2</sup> have good adhesion to the substrate and are free from the discontinuities and defects. The highest percent content of the Al<sub>2</sub>O<sub>3</sub> ceramic phase was observed at the current density of 4 dm<sup>2</sup>(18.6%). The highest microhardness had the coating produced with the cathodic current density of 8 A/dm<sup>2</sup>. The highest wear resistance measured in TWI units had the coating produced with the cathodic current density of 4 A/dm<sup>2</sup>. All coatings had good resistance to corrosion in 1M NaCl environment.

#### Acknowledgements

The study was conducted within the framework of the project entitled "Advanced materials and technologies for their production" Contract with the Ministry of Science and Higher Education No. POIG.01.01.02-00-015/09-00 of 30 December 2009 co-financed by the European Regional Development Fund under the Operational Programme Innovative Economy.

#### REFERENCES

- [1] M. Srivastava, V.K. William Gips, K.S. Rajam, *Materials Letters* **62**, 3487-3489 (2008).
- [2] L. Du, B. Xu, S. Dong, H. Yang, Y. Wu, *Surface & Coatings Technology* **192**, 311-316 (2005).
- [3] P. Indyka, E. Bełtowska-Lehman, M. Faryna, K. Berent, A. Rakowska, *Archives of Metallurgy and Materials* **55**, 2, 421-427.
- [4] B. Szczygieł, M. Kołodziej, *Electrochimica Acta* **50**, 4188-4195 (2005).
- [5] L. Chen, L. Wang, Z. Zeng, J. Zhang, *Materials Science and Engineering A* **434**, 319-325 (2006).
- [6] S.T. Aruna, V.K. William Gips, K.S. Rajam, *J. Appl. Electrochem.* **40**, 2161-2169 (2010).
- [7] R.K. Saha, T.I. Khan, *Surface & Coatings Technology* **205**, 890-895 (2010).
- [8] W. Sheng-Chang, W. Wen-Cheng, *Materials Chemistry and Physics* **78**, 574 (2003).
- [9] Jin-Xing Kang, Wen-Zhen Zhao, Gao-Feng Zhang, *Surface & Coatings Technology* **203**, 1815-1818 (2009).
- [10] A.M. Rashidi, A. Amadeh, *Surface & Coatings Technology* **202**, 3722-3776 (2008).
- [11] Sheng-Lung Kuo, Yann-Cheng Chen, Ming-Der Ger, Wen-Hwa Hwu, *Materials Chemistry and Physics* **86**, 5-10 (2004).
- [12] M. Nowak, M. Opyrchał, S. Boczkal, J. Żelechowski, *Materials Science Forum* **765**, 663-667 (2013).

Received: 10 May 2013.