QUALITATIVE ANALYSIS OF COMPOSITE ZN-PTFE COATINGS

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The aim of this work is to obtain completely new technology of surface treatment. Studies and research in the area of deposition showed that lubricant composite coatings based on zinc with PTFE (polytetrafluoroethylene) particles offer unexpected possibilities of electrodeposition and innovative approach to surface protection. Integral part of this research is a characterisation of applied coatings and it requires the development of reliable methods to determine the coatings´ composition, PTFE content and distribution in the composite coatings. A number of analytical methods were used to characterise all required parameters. Optical microscopy, infrared spectroscopy, Raman spectroscopy, and optical emission spectroscopy were used for characterisation of prepared coatings. Each method proved better or lesser ability to describe tested coating. It is possible to say, that IR spectroscopy allows an easy qualitative analysis of the coatings.

Keywords
Composite coating, Zinc coating, PTFE, IR spectroscopy, Raman spectroscopy

1. Introduction

Composite coatings are used in various fields of industries such as general mechanics and automobiles, electronic components and computers etc. The deposition of finely dispersed particles of PTFE in a metal matrix by electro deposition led to a new generation of composite coatings. These composite coatings show particular physical and chemical properties, which can not be achieved by each component separately.

The main properties which change are wear resistance, self-lubrication, abrasion resistance, and corrosion resistance. These properties depend mainly on type of solution (pH, temperature, bath, etc.) and particles used (graphite, diamond, MoS_2 or PTFE), but also on the concentration, size, distribution and morphology of the particles.

Composite coatings containing PTFE are largely studied in recent time because of their very useful properties such as wear resistance, self-lubrication, etc. [Farias 2009], [Zhao 2004a], [Zhao 2004b] Incorporation of PTFE into composite layer and its characterisation is very important for tribological characterisation. Methods, which can be used for characterisation of composite coatings, are optical microscopy, infrared spectroscopy, Raman spectroscopy, and optical emission spectroscopy. [Serhal 2000], [Serhal 2001] Some of these methods are destructive and require specific preparation of samples. Finding of reliable method to determine the composite coatings composition is necessary for understanding of tribological and corrosion properties.

In this paper, the composite coatings based on zinc and their characterisation was investigated.

2. Results and discussion

2.1. Coatings elaboration

Composite coatings based on zinc and PTFE were coated on sheets of steel with dimension of 50 x 135 x 2.5 mm. Before the zinc plating, the sheets were first cleaned with alkaline solution for 10 min at 45 – 85°C and then rinsed with water. Then activation in dilute HCl solution for 60 s was used and sheets were rinsed with water again. Such prepared sheets were used for electro deposition of composite coatings. The composition of plating solution and zinc plating conditions used are given in Table 1. A 60 wt. % PTFE emulsion with particle size in the range of 0.05 – 0.5 μm was stirred in the bath for 1 h before use. PTFE particles were dispersed uniformly in the bath and floated because of mechanical stirring.

Conditions	Parameters
NaOH	125 g/l
Zn	8 – 15 g/l
PTFE dispersion	1 – 25 vol.%
pH	12
Temperature	20 – 25°C
Current density	3 A/dm^2

Table 1. *Plating conditions*

2.2. Thickness measurement

The coatings thickness was measure by three different methods:

- magnetic method (thickness meter Phynix Surfix v.2.2) – non-destructive method
- gravimetric observation – destructive method
- scratch pattern – destructive method

The deposition rate for different solution composition was determined. The thickness measurement showed that the PTFE content had a significant effect on deposition rate (see Figure 1) – increasing PTFE content decreased the deposition rate.

Gravimetric observation is a destructive method of thickness measurement. Steel sheets with dimensions of 50 x 100 x 1.5 mm were used for coatings application. Dried samples with composite coatings were weighed and then the composite layers were diluted in HCl solution. Steel sheets were rinsed with distilled water, dried, and weighed again. Content of zinc was determined by titration of dissolved composite coating by 0.1 M complexone solution and calculated with following equations.

$$m_{Zn} = a \cdot f \cdot 0{,}006538 \cdot k \qquad (1)$$

m_{Zn} – zinc content [g]
a – 0,1 M complexone solution amount
f – complexone solution factor
k – coefficient (while 20 ml = 10)

$$d_{Zn} = \frac{m_{Zn} .10^4}{S.7{,}1} \qquad (2)$$

d_{Zn} – Zn coating thickness[μm]
S – sample surface [cm^2]
Zinc specific weight – 7,1 g/cm^3

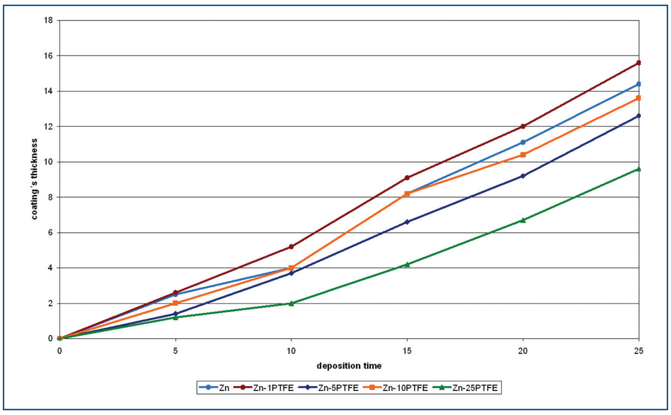

Figure 1. *Effect of PTFE content on deposition rate*

PTFE content in composite coatings was calculated from difference of weight before and after dissolution of the composite coatings reduced for zinc content. It was found that it is not possible to determine the PTFE content less than 5 wt.%.

Results of coatings thickness measurements were compared and can be seen in Table 2. Content of PTFE mentioned in the sample description corresponds to the amount of the dispersion in the plating solution and it does not represent content of PTFE in the coating.

Sample	Deposition time (min)	Phynix Sufix (µm)	Scratch pattern (µm)	Gravimetric observation (µm)
Zn	5	4.2	2.11	
	10	6.3	5.45	
	15	10.4	9.39	
	30	20.2	19.26	18.1
	45	28.2	25.20	
Zn–1PTFE	5	2.6	2.16	
	10	6.6	5.75	
	15	10.4	8.21	
	30	20.0	19.18	17.8
	45	30.8	29.73	
Zn-5PTFE	5	1.8	2.23	
	10	4.7	4.15	
	15	10.0	8.75	
	30	18.0	15.27	13.7
	45	27.0	28.16	
Zn–10PTFE	5	1.8	2.30	
	10	5.4	5.58	
	15	7.8	7.69	
	30	18.7	17.27	15.4
	45	26.3	24.10	
Zn–25PTFE	5	1.7	2.83	
	10	2.6	5.38	
	15	5.1	5.57	
	30	16.0	13.27	12.1
	45	22.6	22.27	

Table 2. *Comparison of thickness measurement results*

2.3. Composition analysis

The surface morphology and coatings composition was analysed by scanning microscope Olympus Lext OLS 3000 with following parameters. Magnification of 120 x – 14 400 x was used and X-Y resolution of 0.12 µm and Z resolution of 0.01 µm. Zn-PTFE coatings cross sections can be seen on Figure 2.

Composite coatings were analysed by Raman spectroscopy and infrared spectroscopy to determine the composition and PTFE content. Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. This method is convenient for substances studying, for structure and composition definition, respectively. PTFE content in the coatings can be explicitly proved by PTFE dispersion, Zn coating without PTFE, and Zn coating + PTFE dispersion spectra confrontation. Measurement was performed by Raman microscope XploRA (Horiba J&Y) with excitation at 532 cm^{-1}.

Figure 3. shows Raman spectrum of PTFE dispersion. The most strong absorption bands are at 733.6 cm^{-1}, two in range from 288.6 to 385.2 cm^{-1} and 477.9 cm^{-1}, respectively and three absorption bands can be found at 1 210.7 – 1 383.9 cm^{-1} range. Detailed information about Raman spectroscopy measurement can be found on previous work [Drasnar 2010].

Infrared spectroscopy is the spectroscopy that deals with the infrared region of the electromagnetic spectrum. The spectrum of samples was recorded by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength and analysis of these absorption characteristics reveals details about molecular structure of the samples.

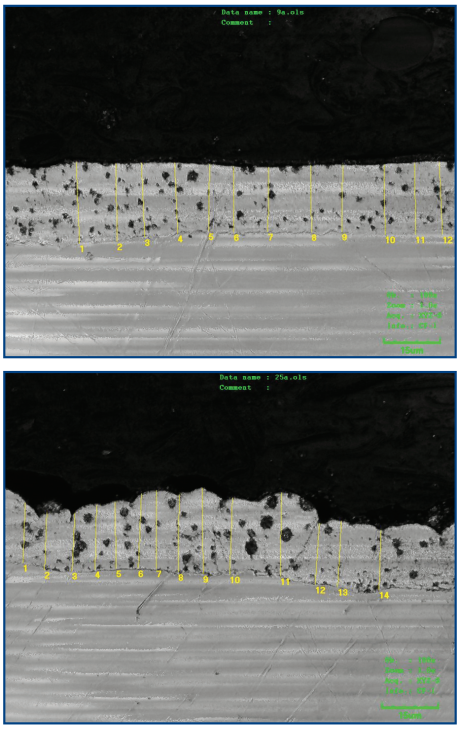

Figure 2. *Photo of Zn-PTFE coatings cross-section (Zn–1PTFE, Zn–25PTFE)*

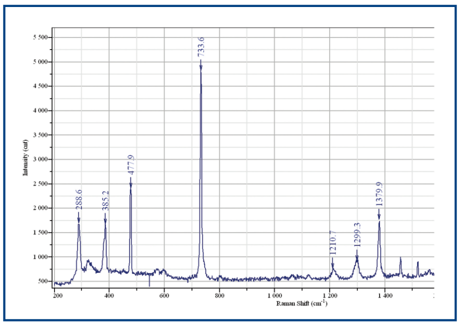

Figure 3. *Raman spectrum of PTFE dispersion*

FTIR spectrometer Nicolet 6700 (Thermo-Nicolet, USA) and microscope Continuum were used for analysis. Parameters of measurement are as follows: 4 000 – 650 cm^{-1} spectral range, resolution of 8 cm^{-1}, number of spectra accumulations 128, apodization Happ--Genzel. With respect to the sample character, beamwidth was adjusted to a small diameter of 3 x 3 µm and number of spectra accu-

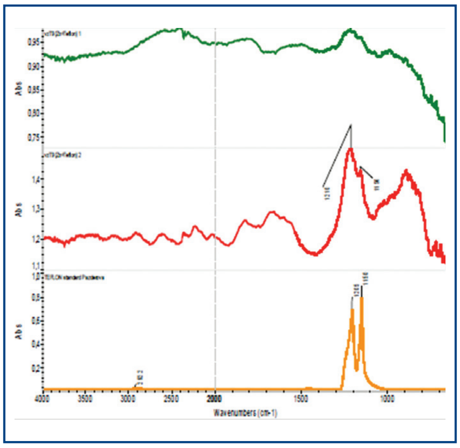

Figure 4. *IR spectrum of Zn-PTFE coating*

mulations was increased proportionally to the beamwidth. Gained spectra were evaluated by Onmic 7.3 (Nicolet Instruments Co., USA) software and identified with using the spectra library.

Figure 4 shows IR spectrum of deposited composite coating Zn-PTFE. Characteristic absorption bands are pointed out and they can be found at 1 210 and 1 156 cm^{-1}, respectively. Yellow line represents spectrum of PTFE dispersion used for the deposition that was used as a standard and the other ones shows the spectra measured at deposited composite coating.

Conclusions

Zinc composite coatings containing PTFE can be prepared by electrodeposition. The current density, stirring rate and PTFE dispersion content in the bath influenced the deposition rate. Increasing PTFE content caused decrease of deposition rate.

A number of analytical methods were used to characterise all required parameters. Comparison of Raman spectra obtained by the examination of all surfaces confirmed the applicability of the method for coatings qualification. This work revealed that the presence of PTFE particles in the composite coatings is made obvious by infrared spectroscopy. Absorption bands of C-F allow an easy qualitative analysis of composite coating.

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