THE PROPERTIES OF ELECTROLYTICALLY DEPOSITED COMPOSITE ZN-PTFE COATINGS

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The requirements for the properties of the surface of highly stressed components are getting increasingly higher so the pure metal coatings are not sufficient any more. The research and development makes it possible to use new alloy or composite coatings which extend the possibilities of surface treatment applications. This study looks at the composite, electrolytically deposited Zn-PTFE coatings (polytetrafluoroethylene) focusing on the manufacturing technology and composition analysis. An optimised technological process results in obtaining a coating of the required properties, i.e. a coating with uniformly distributed content of PTFE particles. It describes the relations between the technological parameters of metal plating and the contents of PTFE in the coating. The analysis of the Zn-PTFE coating composition, i.e. the presence of PTFE has been proved using the method of infrared micro-spectroscopy in the Molecular Spectroscopy Laboratory in the Institute of Chemical Technology (ICT) in Prague. The metallographic tests for the assessment of coating structures were carried out at the Institute of Manufacturing Technology of the Faculty of Mechanical Engineering at Czech Technical University in Prague. The research into the electrochemical composite coatings contributes to the possibilities of producing composite coatings with a wide range of applications.

Keywords

galvanization, zinc, PTFE, composite coating, electroplating, technological process

1. Introduction

The properties of pure metals often do not suit the challenging tribological requirements of the surface layers, so recently composite coatings have been starting to take over the lead. The physical and mechanical properties of the resulting coating are much better that the properties of its individual components. The composite coating, deposited in a process of galvanization, consists of a metal matrix which contains a certain amount of dispersed solid particles. This method benefits from the combination of the different properties of the metal matrix (ductility, electric conductivity, heat conductivity, corrosion resistance) and the properties of the dispersion (extreme hardness, sliding properties). With a suitable combination of components and technological conditions it is possible do produce a precise type of coating which is able to meet even the most challenging requirements. [Kreibich 1999]

Electrodeposited coatings provide anti-corrosive protection to the underlying base material. If we want to combine the requirement for anti-corrosive protection with the requirement for low friction coefficient we can use a multilayer system or a composite coating with dispersed particles which provide a great benefit compared to the multilayer systems: in multilayer systems the suitable tribological properties are provided only by the last layer so the basic properties of the lower layers of the coating are suppressed. The new type of composite coatings based on Zn with the dispersion of PTFE (polytetrafluoroethylene) particles is unique in that the PTFE particles are not only present in the surface layer but are deposited within the whole thickness of the galvanically deposited zinc matrix. Besides, when deposited on steel, this coating provides both the barrier and cathodic protection. So, this coating offers excellent anticorrosive properties together with low friction coefficient without the necessity to provide separate sliding layers.

Previously it was found possibility to create electroplated composite Zn-PTFE coating, both in alkaline [Pazderova 2010] and subacid [Drasnar 2010] zinc bath. It is known, that subacid Zinc bath has good levelling ability, good throwing power and excellent coverage ability. Subacid Zinc baths are characterized by the best quality coatings in electroplating, moreover operational pH of subacid bath has the most user friendly hygienical aspects. It is important, this type of bath has high operation reliability and low operation costs. [Szelag 2010]

For these reasons the objective of the project was to identify the optimum technological conditions for the process of galvanization of steel samples using the Zn-PTFE composite coating in subacid Zincbath. The composition of the Zn-PTFE coating has been analysed, i.e. the presence of PTFE proved, using the method of infrared micro-spectroscopy.

2. Experiment

2.1 Samples

For the experiment we used samples of low-carbon cold-rolled 1008/1010 steel of the following parameters: dimensions 76 x 127 mm and thickness 0.8 mm. The surface was clean so there was no need of any mechanical pre-treatment. The samples were galvanized in a zinc bath containing PTFE.

2.2 Technological process

The experiment was carried out in the laboratory of the electro-plating plant which is located at the Faculty of Mechanical Engineering at Czech Technical University in Prague. The parameters of individual technological operations have been chosen in dependence on the parameters of the used baths. Used general technological process is described by Table 1.

Degreasing	strongly alkaline degreasing agent designed for electrolytic, immersion and ultrasonic-assisted degreasing of items made from steel and nonferrous metals	
temperature	*time*	*current density*
45 ± 5 [°C]	1 [min]	8 [A.dm^{-2}]
Activation	hydrochloric acid (HCl) at the concentration of 100 to 150 g.l^{-1}	
temperature	*time*	
20 ± 2 [°C]	1 [min]	
Galvanization	subacid zinc-coating bath designed for both rack as well as barrel plating. The bath has a good levelling ability, good throwing power and excellent coverage ability.	
temperature	*time*	*current density*
20 ± 2 [°C]	10 [min]	1 [A.dm^{-2}]
Rinsing	rinsing between individual stages (water) – two-phase. Rinsing after galvanizing– demineralised water.	
temperature	*time*	
20 ± 3 [°C]	0.5–1 [min]	
Drying	hot air drying of galvanized samples.	
temperature	*time*	
50 ± 5 [°C]	2 [min]	

Table 1. *General technological process of electroplating*

Bath composition

The content of individual components of the bath is reduced in the course of the galvanisation process by being removed together with finished products and by electrochemical consumption. Due to the imbalance of the current yield, anodes melt more zinc than deposited on the cathode so it is not necessary to replenish any zinc chloride. Potassium chloride and boric acid are replenished based on analysis.

First we tested the bath without adding any tensides or gloss-enhancing ingredients. The deposited Zn coatings are rugged and incoherent. Besides, it was not possible to measure the thickness of such a deposited coating. That is why we enriched the solution with a mixture of low-foaming surface-active tensides and dispergators with the concentration of 20 ml.l^{-1} and further even 40 ml.l^{-1}. The surface-active tensides reduce the surface tension and prevent the development of hydrogen pores. Only with tensides added into the bath it is possible to produce semi-gloss coatings with satin gloss. High gloss coatings can be achieved by adding brightener. It contains components which only influence the appearance properties of the deposited coating. The degree of brightness is dependent on the amount of the brightener added into the bath.

The last component that was used was PTFE dispersion. PTFE particles tend to deposit on the bottom of the bath tank, so mixing must be provided during the whole process of metal-plating. The process of galvanization was carried out in laboratory galvanizer which allowed mixing the bath solution via a pump. Zinc bath operating conditions are shown in Table 2.

Bath parameter	Ranges allowed for rack galvanization
Cathodic current density [A.dm^{-2}]	0.5 – 7
Anodic current density [A.dm^{-2}]	0.1 – 2.5
Bath voltage [V]	2 – 8
Bath temperature [°C]	15 – 45
Bath pH	4.5 – 5.4
Deposition rate	1 µm.min^{-1} at 4 A.dm^{-2}

Table 2. *Subacid zinc bath operating conditions*

2.3 Analysis of the surface layer of the Zn-PTFE coating

2.3.1 Infrared spectroscopy

Infrared spectroscopy is an analytic method used mainly for the identification and examination of organic compounds and inorganic substances. It makes use of the ability of the analysed substances to absorb infrared radiation of various wavelengths. This makes changes to the rotation and vibration of the molecule in dependence on the changes to the dipole moment of the molecule. Infrared radiation is electromagnetic radiation with wavelengths ranging 0.78 to 1000 mm, which correspond to the wavenumber range of 12 800 to 10 cm^{-1}. [Machovic 2011]

The output of the analysis is an infrared spectre which is expressed graphically as a relation of energy to the wavelength of the incoming radiation. Energy is expressed, for example, in the units of absorbance (A), expressed mathematically as the negative common logarithm of transmittance (log 1/T). Transmittanceis the ratio of the intensity of the light that has passed through the sample to the intensity of the light when it entered. As the energy/wavelength relation is logarithmic, we use the inverse of the wavelength – wavenumber. The relation of energy to wavenumber is linear. [Machovic 2011]

The analysis was carried out using the FTIR spectrometer Nicolet 6700 (Thermo-Nicolet, USA) together with the Continuum microscope (Molecular Spectroscopy Laboratory in the Institute of Chemical Technology (ICT) in Prague), reflectance measurements, MCT detector, parameters of the measurements: spectrum range 4000 – 650 cm^{-1}, resolution 8 cm^{-1}, number of spectra accumulations 128, Happ-Genzelapodization. Gained spectra were evaluated using the Omnic 7.3 (Nicolet Instruments Co., USA) software and identified using the spectral library. [Novotna 2011]

With respect to the sample character, the beamwidth was adjusted to a small diameter of 3x3 µm, and the number of spectra accumulations was increased to 1024proportionally to the beamwidth. 3 spectra were measured in each sample. [Novotna 2011]

Homogenous distribution of PTFE in the surface layer of the composite Zn – PTFE coating is illustrated in Figure 1 providing a detail view of the spectral range 1300 – 1000 cm^{-1}. Homogenous distribution of PTFE in the surface layer is documented by almost identical intensity of the absorption bands representing the vibrations of the PTFE -CF_2 groups.

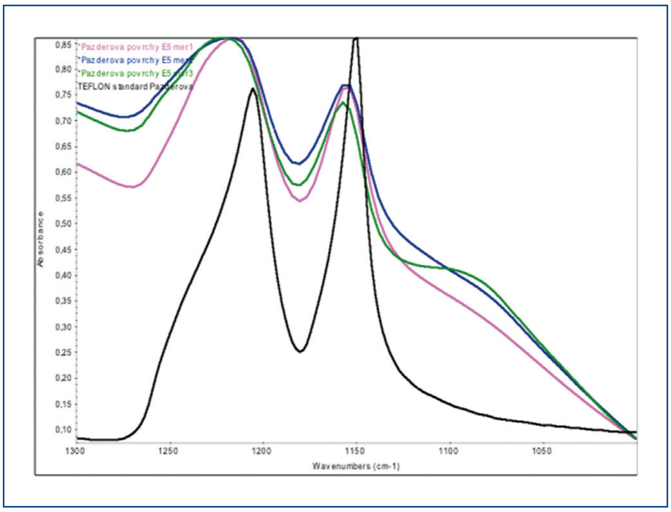

Figure 1. *IR spectre of the Zn-PTFE composite coating with almost homogenous distribution of PTFE in the surface layer*

Using the method of infrared spectroscopyit is possible to demonstrate the presence of PTFE particles in the electrolytically deposited Zn-PTFE composite coating by comparing the measured spectra of the coating to the spectral library.

2.4 Zn-PTFE coating cross-section analysis

Besides examining the surface layer of the coating for the presence of PTFE particles we wanted to find out whether it will be possible to prove the presence of these particles within the whole thickness of the deposited coating. To analyse the composition of the Zn-PTFE composite coating we used the Axio Observer D1m optical microscope by Carl Zeiss (Institute of Manufacturing Technology of the Faculty of Mechanical Engineering at Czech Technical University in Prague).

Figure 2 (left) shows a polished section of zinc coating including its measured thickness. A polished section of the composite Zn coating containing 10 % PTFE can be seen in Figure 2 (right) showing large dark formations which may be bunches of PTFE particles.

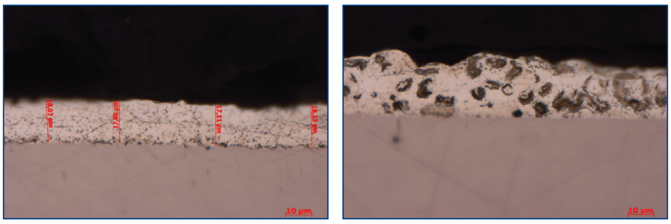

Figure 2. *Electrolytically deposited coating of Zn, magnified 500 times (left), composite coating of Zn – 10 % PTFE, magnified 500 times (right)*

2.5 Effect of PTFE articles on the deposition rate of the zinc bath

The effect of PTFE particles on the deposition properties of the zinc bath was demonstrated by comparing the deposition rates of the

Zn and Zn-PTFE baths. The deposition rate of the electrolytic bath *v* [μm.s^{-1}] is expressed as a ratio of the coating thickness *h* [μm] to time *t* [s]. The thickness of the coating was measured using the Elcometer 456 digital coating thickness gauge. Steel samples were measured at 10 sites from all sides to cover the whole surface of each sample. These measurements were used to calculate the average thickness of the deposited layer. The samples rested in the zinc bath for 5, 10, 15, 20 and 25 minutes featuring the same concentration of tensides and gloss-producing ingredients and equal technological conditions.

The deposition rates in pure zinc and Zn-PTFE coatings are linear. Thin Zn coatings are not widely used in practice so we did not examine deposition rates for the period shorter than 5 minutes. Figure 3clearly shows that 10% concentration of the PTFE particles has no substantial effect on the deposition rate, which is approx. 0.55 μm.min^{-1}.

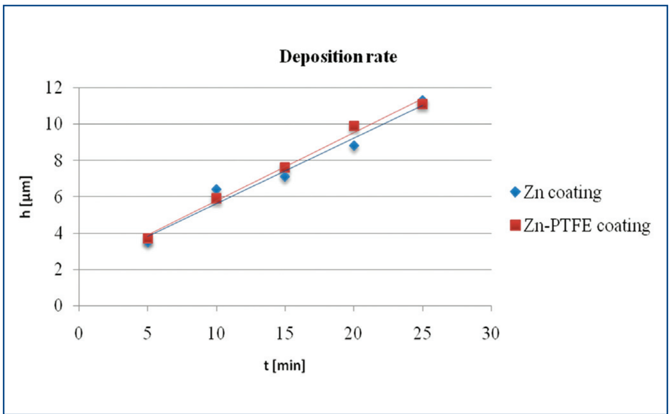

Figure 3. *Graphical representation of the deposition rate of Zn and Zn-PTFE (10 %)*

2.6 Identification of the optimum technological parameters of Zn-PTFE baths

As there are plenty of factors which influence the final results of the electroplating process we divided our research into several experiments which we carried out while making changes the following conditions: current density, deposition time, bath temperature, bath pH, concentration of PTFE, concentration of tensides, presence of gloss-producing additives and the mixing method. Gradually, we found for each variable the range of values ensuring the best properties of the analysed sample. The purpose of these experiments was to identify the optimum conditions for the electrolytic deposition of the Zn-PTFE composite coating on the basis of infrared micro-spectroscopic analysis, the method of measurements on polished sections and visual assessment.

List of monitored parameters:

- presence and concentration of tensides in the Zn bath;
- addition of gloss-producing ingredients intothe Zn bathcontaining 40 ml.l^{-1}of tensides;
- effects of PTFE concentration in the Zn bath on the amount of PTFE found in the deposited coating;
- mixing method–interrupted withintervals of 10 to 15 s, continuous, manual;
- current density ranging from 0.5 to 2.5 A.dm^{-2};
- deposition time;
- bath temperature ranging from 16 to 28 °C;
- bath pH 4.5 ± 0.01 and 5.5 ± 0.01.

3. Conclusions – assessment of the properties of the coatings

The objective of the research work was to identify the optimum technological conditions for the process of electroplating steel samples with the Zn-PTFE composite coating. The suitability of individual technological conditions was assessed on the basis of an analysis using the method of infrared micro-spectroscopy. Besides the analysis of the surface layer by the method of infrared micro-spectroscopy, optical microscope was used to examine polished sections of the samples. Another test compared the deposition rate of a pure Zn coating to the deposition rate of the Zn-PTFE composite coating while assessing the appearance properties of the coatings.

During the process of electroplating in the Zn-PTFE bath we had to ensure that the solution is mixed properly to prevent the PTFE particles from settling on the bottom of the tank. Mixing also facilitated the transport of PTFE particles to the surface of the object being electroplated. In terms of concentration and distribution of the particles in the coating the most suitable current density was identified within the range of 1.5 to 2 A.dm^{-2} and the time of electroplating should not exceed 20 minutes. The temperature of the bath is connected with the pH which should range between 4.8 and 5.5. For pH values close to 5.0 the optimum temperature is 19 ± 1 °C, for higher pH values of up to 5.5 the upper temperature limit may be increased to 22 C. A coating with homogenous distribution of PTFE particles of high concentrations was deposited at the temperature of 21.5 °C, electroplating process duration 10 min, current density 1.5 A.dm^{-2} and bath pH value 5.51.

By examining the surface layer of the coatings using the method of infrared micro-spectroscopy it is possible to prove without any doubts the presence of PTFE particles in the Zn-PTFE composite coating and to gain insight into the concentrations and distribution homogeneity. In order to be able to examine the composition of the composite coating using a metallographic optical microscope, polished sections were prepared.

The photos of the pure Zn coating and the Zn-PTFE composite coating show different structures which can be identified as bunches of PTFE particles. The measurements of deposition rates revealed a linear relationship between the thickness of the coating and the duration of the electroplating process. Another very significant finding was that the 10% concentration of PTFE particles has no effect on the deposition rate compared to the pure zinc coating. The experiment also proved that the addition of gloss-producing ingredients into the bath has no effect on the deposition of PTFE particles in the coating. Thus, it is possible to develop a Zn-PTFE composite coating with high-standard appearance properties.

The follow-up experiments carried out within the research into the Zn-PTFE composite coating involve tribological tests. They could focus on adding the finishing procedure of chromate treatment into the technological process. Also, it is necessary exactly to examine the effect of PTFE particles on the corrosion resistance of the coating.

This coating is presumed to be used on high-strength bolts featuring high corrosion resistance and low tightening torque.

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