Composite Zn-PTFE coatings

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Abstract

This paper covers the development of a zinc-polytetrafluorethylene (Zn-PTFE) coating. Zn-PTFE plating was based on zinc electrolytic plating in weakly acid bath. The influence of process parameters on the incorporation of PTFE particles into zinc matrix was studied by infrared spectroscopy and tribological measurements. Thus we have determined the optimal setting of the technology conditions and as a result we have obtained coatings joining the corrosion protection properties of zinc coating with lubricating properties of PTFE. The potential of Zn-PTFE coating is seen in their application on bolts etc. as an advantageous replacement of existing coating systems with lubricating properties.

1. Introduction

We have worked on the development of electroplated zinc coating with enhanced tribological properties. Motivation for commence of this project resulted from the following situation in the field of metal plating. Zinc electroplating represents the most widely used surface treatment in mechanical engineering, including aerospace and automotive applications. Its share is about 20 % in the Czech Republic and it is similarly high in the rest of European countries [1]. The benefit of the use of electroplated zinc coatings is in the relative simplicity and reasonable cost of their production, and mainly in their excellent corrosion protection properties. However, there have recently been increasing demands on additional properties of the coatings, e.g. on their friction coefficient and wear resistance. These demands come from aircraft and automotive industry, as well as other industries [2]. Existing ways of dealing with the demands are in the application of multilayered electroless coating systems, e.g. zinc coating topcoated with passivate and finally sealed with a lubricated post-treatment are used [2]. These technologies have a few disadvantages, e.g. the imprecise fit of structural elements caused by high thickness of final coatings and the complexity of the coating procedure resulting in high economical, power and time requirements. The solution of this is seen in the technology of composite coatings combining zinc coating with dispersed particles, e.g. PTFE. This has led us to the development of a new Zn-PTFE composite plating based on the successfully used technology of zinc electroplating.

In general, composite coatings consist of matrix and different types of particles dispersed in it. The combination of components properties gives rise to specific mechanical, physical and chemical properties which can not be achieved by each component separately [3]. The incorporation of PTFE particles into the metal matrix provides enhanced tribological properties because of extremely low friction coefficient, non-stick and self-lubricating properties of PTFE. Metal or metal alloy coatings containing PTFE particles can be prepared by electroless or electrolytic plating. The later process is simpler, can be easier controlled and operated at room temperature. Conversely, there are often difficulties concerning inhomogeneous thickness of electrodeposited coating, low content of incorporated particles and their non-uniform distribution in the coating [4, 5]. The electroless plating composite coatings such as Ni-P-PTFE-SiC, Ni-Cu-P-PTFE and Ag-PTFE have been described in the literature [6, 7, 8]. Electroplating of composite coatings, e.g. Au-PTFE [9], Ni-P-PTFE-SiC [10], Ni-P-TiO_2-PTFE [11] and Re-Ni-W-P-SiC-PTFE [12] is known as well. However, to our knowledge, there has been no reference to electroplated Zn-PTFE coating. Research and development in the area of zinc electrolytic plating deal mainly with the improvement of corrosion resistance properties and ecological safety of the technology rather than with the innovations of tribological characteristics.

The technology of Zn-PTFE coating synthesis was based on the technology of the electrolytic galvanising process in weakly acid bath and the electrolytic process of Ni-P-PTFE coating deposition. Ni-P-PTFE coating has excellent sliding properties even under high temperatures and mechanical stresses. On the other hand, the cost of basic material is higher than that for Zn-PTFE coating. Moreover, regarding the corrosion protection, nickel coating has only barrier effect while zinc coating acts as sacrificial anode because it is a less noble metal than iron.

It is necessary to obtain coatings with sufficient amount of incorporated PTFE particles homogeneously distributed in the coating to ensure improved tribological properties of metal coating. Generally, the content and homogeneity of PTFE depend on the conditions of the plating process. We considered the influence of these conditions: the concentration of PTFE particles in the bath, pH and temperature of the bath, the value of applied current density, plating time and the mode of stirring. We tried to evaluate their impact on the coating properties using infrared spectroscopy and tribological measurements.

The application of Zn-PTFE plating is seen in the production of bolts and nuts (i.e. bolt joints) as it can fulfil the requirements on the surface treatment of bolts, such as i) proper corrosion resistance, ii) necessary bolt preloading, iii) easy dismantling and iv) prevention of a bolt seizure [13]. Other applications can be friction bearings, sliding joints etc.

2. Materials and methods

Mild steel sheets (50 x 135 x 2.5 mm) were used as substrates. Substrate pretreatment consists of these successive steps - degreasing in basic solution, etching in hydrochloric acid (HCl), electrolytic degreasing in alkaline solution and activating in diluted HCl. After each step the sheets were rinsed with running tap water, hot for alkaline solutions, cold for acid ones. Weakly acid bath for zinc plating was used with the addition of various amounts of 60 wt% PTFE dispersion (particle size in the range of 0.05 to 0.5 μm). A dispersant in the concentration of 40 ml/l and a brightener in the concentration of 3 ml/l were added to the bath.

The plating was run as hanging plating with supplied cathodic current. A Robbe No. 3985 Potentiostat/Galvanostat (Robbe GmbH & Co. KG, Germany) was used as a power supply. The mild steel sheets were used as cathodes and zinc sheets as anodes. An anode-to-cathode area ratio was 1-2 to 1. The bath was stirred for 60 min prior to each experiment. The agitation was done by means of air coming through perforated tube which was placed in the horizontal position at the bottom of the bath. The parameters of plating - PTFE concentration, current density, deposition time, pH, temperature and mode of stirring - were changed and recorded during the experiments.

The composition of the coatings was determined by FTIR spectrometer Nicolet 6700 (Thermo-Nicolet, USA) with microscope Continuum. The IR measurements were taken at three different locations on the steel sheets (top, centre, and bottom) to study the homogenity of the coating. Tribometer TOP3 (experimental device of the Czech Technical University in Prague) was used to analyze the tribological properties of the coatings. Friction pair was formed by “area (tablet) – area (plate)” and coatings were deposited on both components. The thickness of coatings was measured by non-destructive method using coating thickness gauge Surfix® (Phynix GmbH & Co., Germany). Confocal laser scanning microscope Olympus Lext OSL 3000 (Olympus Co., Japan) and optical microscope Fiber Optic Illuminator System (Cole-Palmer, USA) were used to characterised the morphology of the coatings.

3. Results and discussion

3.1 Influence of the process conditions on Zn-PTFE coating properties

Process conditions of Zn-PTFE plating were based on the working parameters of acid zinc bath, which were given by its manufacturer. It was necessary to consider the effect of the parameters on the quality as well as on the performance of prepared Zn-PTFE coatings. The former pertained to the quality of zinc coating itself (e.g. adhesion to the substrate) and to the incorporation of PTFE particles into the coating. The later pertained to the friction characteristics of the coatings.

The influence of the parameters was evaluated using IR spectroscopy and tribological measurements. IR spectroscopy enabled to determine the presence of PTFE in the coating based on the presence of PTFE characteristic absorption bands in the spectrum of the coating. These bands occur at about 1157 and 1217 cm^{-1} and correspond to streching vibrations of C-F bonds in PTFE. Moreover, it was used to make relative comparison of the quantity of incorporated PTFE in coatings. This was done by the comparison of the areas under the bands, i.e. the integral intensities. The friction characteristics were expressed as friction coefficients and wear resistance of the coatings. The parameters were varied in specific range (Table 1).

Table 1: Range of the parameters used for the preparation of Zn-PTFE coating

PTFE concentration	1 – 10	[%]
Current density	0.5 – 3	[A/dm^2]
Time	10 – 30	[min]
pH	4.5 – 5.5	--
Temperature	16 – 28	[°C]
Mode of stirring	continuous / intermittent / combination	

Influence of current density

Figure 1 shows IR spectra of four coatings prepared under different current density values while other parameters values were kept constant. Curves in each spectrum correspond to measurements at three different places of the sample. Comparing the integral intensities of C-F bands, the influence of current density value on PTFE content in the coating was evaluated. It was found that with increasing current density the PTFE content increased as well. However, there is a drawback of this evaluation lying in the inhomogeneity of the PTFE distribution. Regarding the fact that there are pronounced absorption bands on two curves for current densities 1 and 1.5 A/dm^2, it can be claimed that PTFE particles were spread more homogeneously throughout the coating when lower current densities were applied.

The current density of 1.5 A/dm^2 was finally chosen as an optimal value for the preparation of the coatings since when combined with different process parameters than those used in this experiment; the best incorporation of PTFE into the coating was reached (Fig. 3b). Moreover, this selection was supported by tribological results which showed that Zn-PTFE coatings prepared at higher current densities (2.5 A/dm^2 and higher) had worse dynamic coefficient than zinc coating without PTFE and had almost none wear resistance (data not shown).

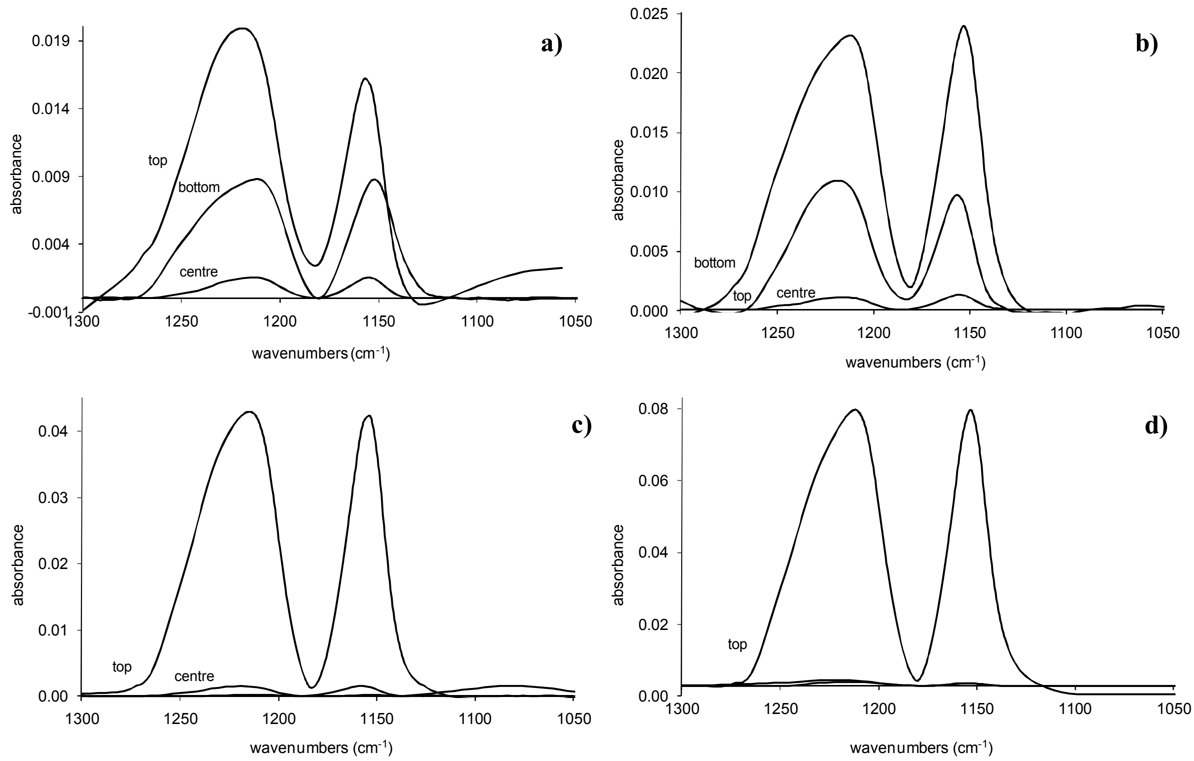

Figure 1: IR spectra of Zn-PTFE composite coatings prepared under these conditions {10 min, 19.5 °C, pH 4.88, intermittent stirring} and at different current densities: a) 1, b) 1.5, c) 2 and d) 2.5 A/dm^2.

Influence of temperature

The effect of temperature on the PTFE incorporation in the coatings was also evaluated by comparing the areas under the PTFE bands in the IR spectra (Fig. 2). The results showed that the deposition at lower temperatures had a positive effect on the PTFE particles integration into the coatings. The content of PTFE in the coating was the highest for sample prepared at 20 °C and the second highest for sample prepare at 16°C. Although the temperature dependence is not directly proportional as evident from the results, a "cut-off point" at 22°C was estimated separating a positive and negative effect on the PTFE content in the coatings prepared below and above 22°C, respectively.

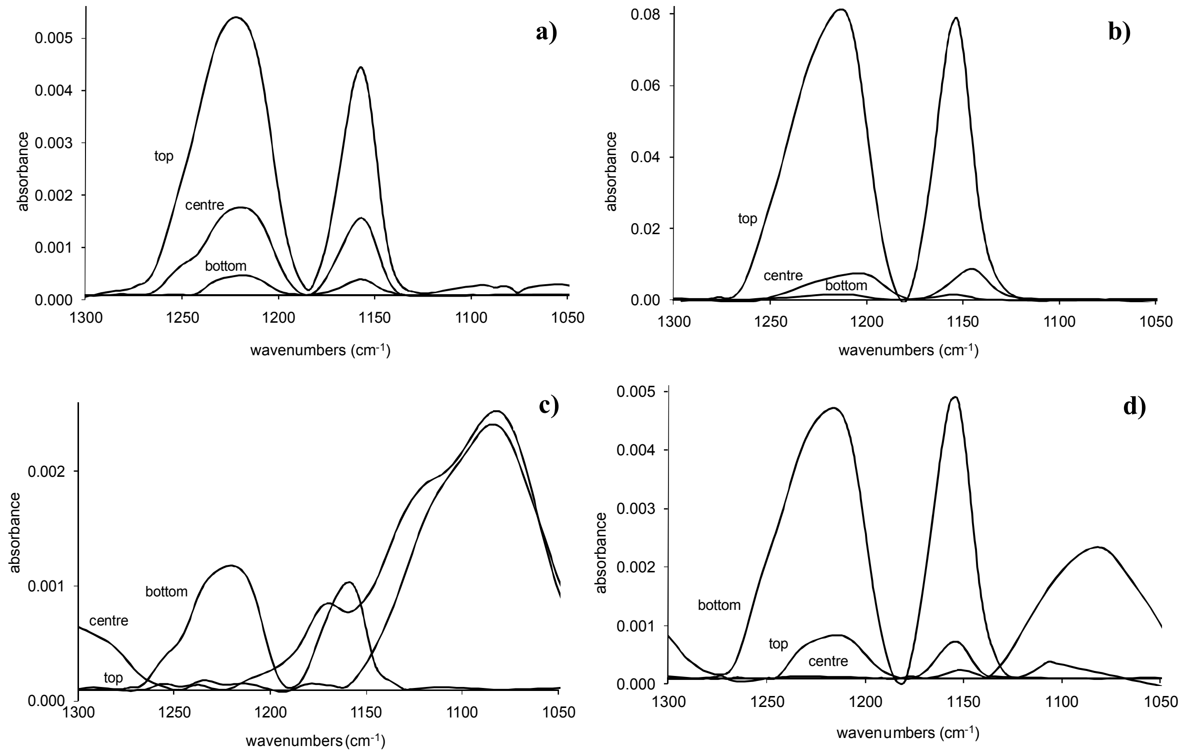

Figure 2: IR spectra of Zn-PTFE composite coatings prepared under these conditions {1.5 A/dm^2, 10 min, pH 5.16, continuous stirring} and at different temperatures: a) 16, b) 20, c) 24 and d) 28°C.

Influence of PTFE concentration, pH, plating time and mode of stirring

The aforementioned results and the results of experiments aimed at the influence of other process parameters enabled us to make closer specification of suitable combination of parameters to prepare Zn-PTFE coatings of high quality. Spectra in Fig. 3 (only the selection of the results is displayed) show that PTFE content was higher and its distribution was better for those coatings prepared under the conditions used for the preparation of the coating b) than coating a). On this basis the following values of parameters were chosen.

The optimal concentration of PTFE in the bath was found to be 10% because higher concentration of PTFE in the bath resulted in higher PTFE content in the coating. Findings were confirmed by tribological measurements (chapter 3.2). Higher concentrations of PTFE were tested as well; however, such amount of PTFE dispersion in the bath proved to make the stirring less efficient and the cost of the final coating would also get needlessly higher. Concerning the influence of pH of zinc acid bath, values between 5.00 and 5.50 were chosen for Zn-PTFE electroplating. The parameter of time served to the adjustment of coating thickness. The experiments showed that ten minutes long deposition produced coatings 5 - 8 µm thick depending on other applied parameters. A significant effect on the homogeneity of PTFE particles distribution in the coating had the mode of stirring. It was found that the distribution of the particles in the coating was more homogeneous when continual stirring rather than intermittent stirring or their combination was applied.

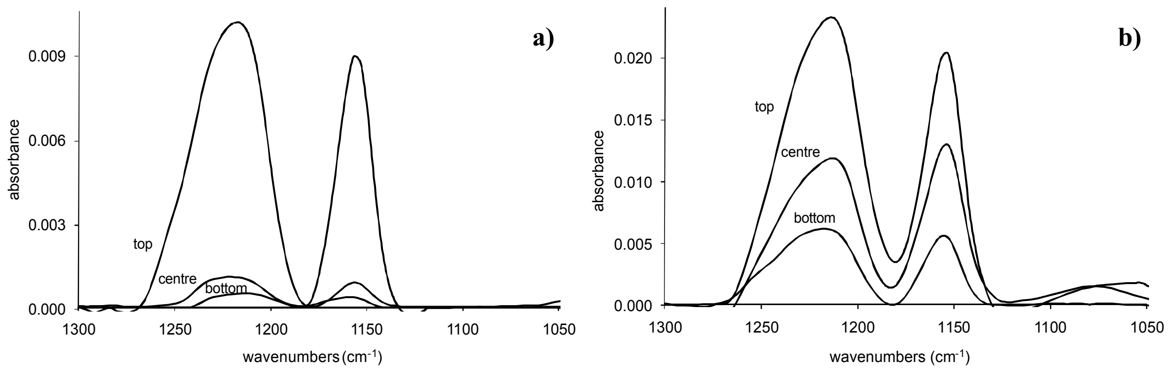

Figure 3: IR spectra of Zn-PTFE composite coatings prepared under these conditions a) {1.5 A/dm^2, 20 min, 10% PTFE, 20.8°C, pH 4.50, intermittent stirring}, b) {1.5 A/dm^2, 10 min, 10% PTFE, 21.5°C, pH 5.50, continuous stirring}

The surface morphology image and the microscopic image of the cross-section of the coating prepared under the same condition as the one in Fig. 3b) are displayed in Fig. 4 and 5, respectively. Figure 4 demonstrates the different morphologies of zinc coating with PTFE and zinc coating without PTFE. Black particles present in the upper layer of the coating in the cross section images are the PTFE particles (Fig.5).

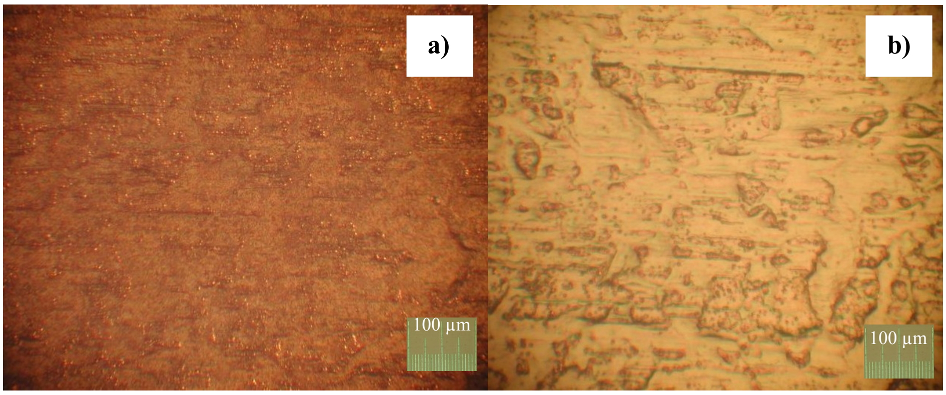

Figure 4: Surface morphology of a) Zn-PTFE coating and b) zinc coating both prepared under the same conditions with and without PTFE, respectively.

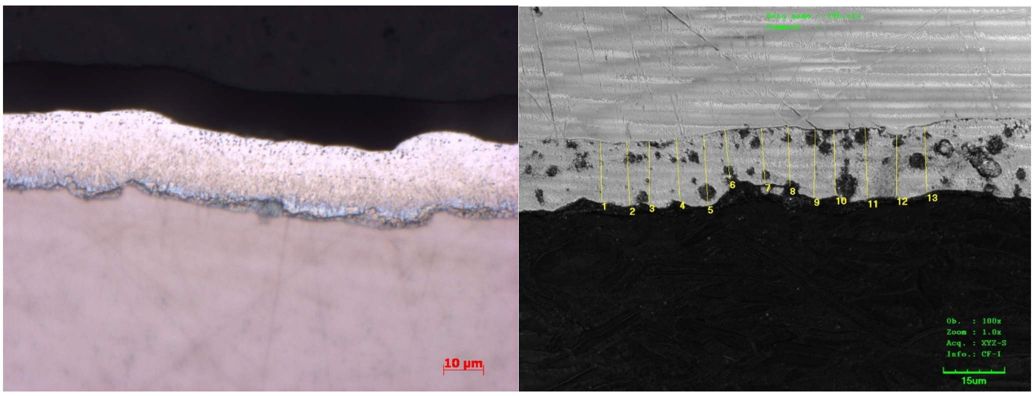

Figure 5: Microscopic cross-section images of Zn-PTFE coating.

3.2 Tribological properties of Zn-PTFE coating

The quality of prepared coatings was also evaluated by tribological measurements. Friction coefficient as a main parameter of Zn-PTFE coatings was measured for different arrangements of friction pairs and it was compared with the friction coefficient of zinc coating – zinc coating pair (Fig. 4). The lowest value of the static (f_s) and dynamic (f_d) coefficient had Zn10PTFE-Zn[1] pair and the second lowest Zn3PTFE-Zn pair. This was obviously because of higher

[1] Note that Zn10PTFE and Zn3PTFE stand for zinc coating prepared from acid zinc bath containing 10% and 3% of PTFE, respectively.

content of PTFE in the Zn10PTFE coating. Contrary to this, higher PTFE content has negative effect on the wear resistance of the coatings (Fig. 5). The effect of PTFE on the reduction of coatings hardness has been reported in the literature [7]. The wear resistance of the coatings is expressed as the decrease in the weight of the coating and as the time of coating durability during the tribological experiment. It can be seen that Zn10PTFE - Zn10PTFE pair has the lowest wear resistance and the Zn10PTFE – Zn pair the second lowest.

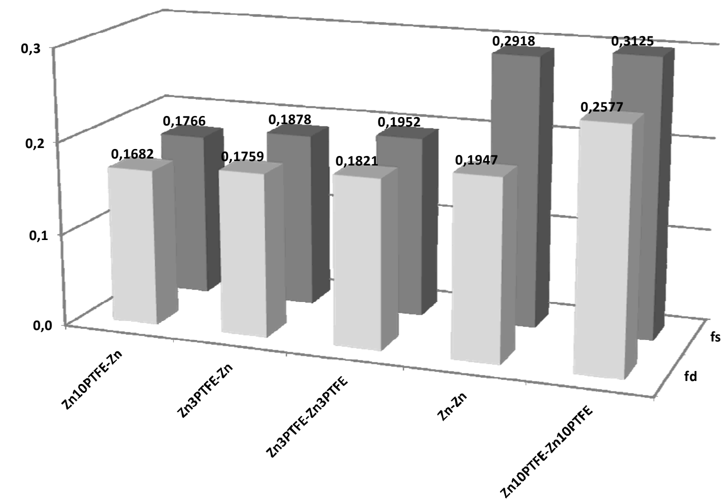

Figure 4: Dynamic and static friction coefficients of zinc and Zn-PTFE coatings

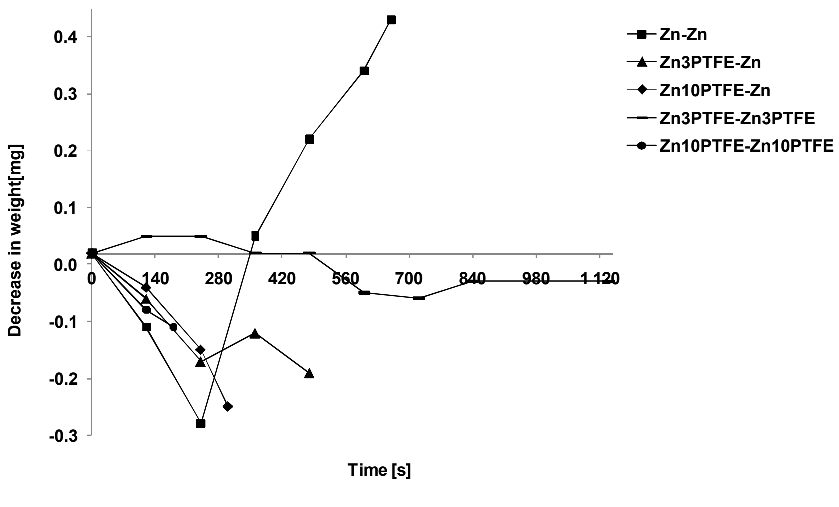

Figure 5: Decrease in the weight of zinc and Zn-PTFE coatings during tribological measurements

4. Conclusion

The results from this study show that it is possible to synthesize Zn-PTFE composite coating based on the technology of zinc electrocoating deposition from weakly acid bath. Moreover, we selected a close range of values of the process parameters which resulted in the homogeneous distribution of the PTFE particles in the zinc coating matrix. Prepared coatings had significantly lower friction coefficients than pure zinc coating. Although the self-lubricating properties of the coatings were improved, the wear resistance of coatings with high content of PTFE was reduced. Therefore, further research will deal with improvement of this tribological characteristics.

This work was carried out in the framework of the projekt FR-TI1/047 of the Ministry of Industry and Trade of the Czech Republic.

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