

THERMAL STABILITY OF PHOSPHATE COATINGS ON STEEL

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The work was validated thermal stability of zinc, manganese and tri-cations phosphate coatings on steel, made from commercial phosphating bath type Pragofos. Thermogravimetric data dehydration of scholzite, phosphophyllite and hureaulite coatings in the temperature range 160 °C – 400 °C define the conditions for applying paints with higher firing temperature or thermal spraying ceramic coatings.

Key words: steel, phosphates, coatings, structure

INTRODUCTION

Phosphating is a simple, cheap and popular technology of a preliminary coating of carbon steel, zinc, magnesium, cadmium and often also aluminium. Thanks to their porosity, deposited coatings of insoluble tertiary phosphates enhance the bond between metal and subsequently applied paint, oils and lubricants. During the application of paint on the surface of a phosphated substrate, these conversion coatings provide better resistance against corrosion under paint. In an automotive industry, phosphating has been considered for many decades the topmost standard of surface pre-treatment prior to the application of paint. Together with appropriate lubricants, phosphate coatings facilitate running-in of rotating machine parts, decrease drag friction and also reduce the risk of seizure of coated gear wheels.

Based on cations contained in a coating bath, phosphating processes can be divided into corresponding categories. Iron, zinc, zinc - calcium and manganese phosphating processes are known. A special process called tri-cationic phosphating is known as well [1].

The most frequently used process is zinc phosphating. During this process, a crystalline coating formed mainly by hopeite $Zn_3(PO_4)_2 \cdot 4H_2O$ is deposited from the bath containing zinc dihydrogen phosphate. The part of the coating closer to the steel surface is formed by a smaller quantity of phosphophyllite $Zn_2Fe(PO_4)_2 \cdot 4H_2O$.

Another phosphating process forming the coating contains mixed zinc-calcium phosphate (scholzite) $Zn_2Ca(PO_4)_2 \cdot 4H_2O$. Manganese phosphating is typical for the formation of a very thick and dense crystalline coating of hureaulites $(Mn,Fe)_3H_2(PO_4)_2 \cdot 4H_2O$ [2].

A very specific method is the so-called tri-cationic or “three-cations” phosphating. A coating bath contains

lower amount of zinc dihydrogen phosphate which is complemented by cations of Ni^{II} , Mn^{II} , Co^{II} or Mg^{II} type. This composition of the coating bath yields a coating formed by the phosphophyllite structure only. The advantage of the phosphophyllite structure is its increased resistance against alkali attack or increased resistance against corrosion under paint.

There are also differences in thermal stability, i.e. in resistance against dehydration. The problem is that the majority of studies using thermo-analytic methods are focused on manganese phosphate coatings only. Relevant data on thermal stability of other coating types are missing or the results are contradictory.

When observing the dehydration of hureaulite coatings it was found out that dehydration takes place only when the temperature of 300 °C is reached and that the total coating weight loss is only 1,27 wt. % [1]. Different results are interpreted in works [3], where the primal dehydration of the hureaulite coating takes place at the temperature between 150 °C and 325 °C with the crystalline structure of the manganese phosphate losing up to three molecules of water. The second dehydration takes place above 325 °C. After the complete dehydration at 350 °C, the anhydrite $Mn_3(PO_4)_2$ and a small amount of Mn_2O_3 were found in the coating, the total weight loss being 12,5 wt. %. In this work it was found out that further weight loss takes place at 535 °C. This causes partial decomposition of manganese oxides. In work [4], the first dehydration of hureaulite is observed at 295 °C, the second at 325 °C. Authors further observed the conversion of anhydrite $(Fe,Mn)_3(PO_4)_2$ to a paracrystalline phase $Fe_{0,5}Mn_{2,5}(PO_4)_2$ at 340 - 400 °C.

Hopeite coatings were studied in work [5], which confirmed that the first dehydration of hopeite takes place already at 115 °C. The formed dihydrate decomposes and forms anhydrite at 317 °C. Authors in [5] say that the primal dehydration of the hopeite coating does not take place before the temperature reaches 160 °C. The dehydration of anhydrite takes places at temperatures close to 270 °C.

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Today, phosphate coatings are also tested as an inter-layer improving corrosion resistance of steels with a plasma deposited ceramic coatings [6].

EXPERIMENTAL PART

Thermal stability of phosphate coatings was studied using a differential thermal analysis (DTA) and thermo-gravimetric analysis (TG) applying Setaram DSC 131 analyser. Both measurements were made in a temperature range between 20 and 400 °C, with heating rate of 10 °C/min in air. The air flow was 25 ml/min in case of DTA and 20 ml/min in case of TGA. For the purpose of the experiment, steel sheets of the first series (120 x 80 x 2 mm) were used. The composition of substrate steel measured by XRF spectrometer ARL 9400 XP is presented in Table 1.

Table 1 Content of impurities in the substrate steel / wt.%

Element	1. series	2. series
Al	0,053	0,034
Si	0,051	0,085
P	0,011	0,013
S	0,018	0,011
Cr	0,043	0,038
Mn	0,735	0,322
Cu	0,088	0,076
Zn	0,027	0,031

The second series of samples, which was also used for SEM image analysis (TESCAN Vega 3-LMU), consisted of smaller steel samples (50 x 20 x 1 mm). The composition of samples is also presented in Table 1. Both types of steel contained approximately 0,1 wt. % of carbon.

For DTA and TG analysis, smears of phosphate coatings were prepared mechanically. An average weight per unit area of phosphate coatings was at Zn - phosphate 21,25 g/m², Mn-phosphate in 15,36 g/m². Zn - Ca - phosphate coating under the same conditions showed a value of 2,81 g/m² and tri-cation phosphate 1,75 g/m² only.

Other samples from the 2nd series were used for a statistically evaluated gravimetric analysis. Ten samples of each phosphate coating were measured. The samples were exposed for 24 hours in a dry static laboratory atmosphere with temperature close to that of the first dehydration (approx. 180 °C, determined from the results of DTA and TG).

Prior to the coating, steel substrate was pre-treated by blasting using corundum (B220) and degreased in alkali bath with active surfactants. After these operations, activation acid etching in 3 wt. % HCl solution followed. The aim of the etching was to neutralize a residual degreasing alkali solution that may stain the surface of samples and slightly increase the surface roughness. For phosphating, 4 different commercial phosphating baths (Pragofos Pragochema Ltd. Prague)

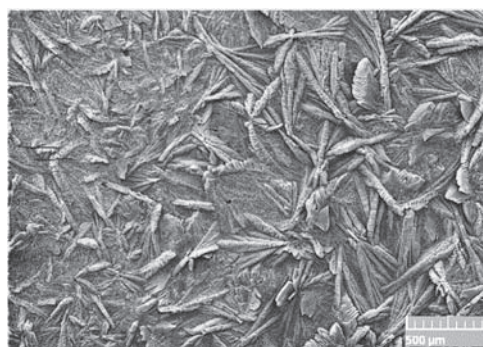


Figure 1 Hopeite coating on steel obtained from zinc phosphate bath

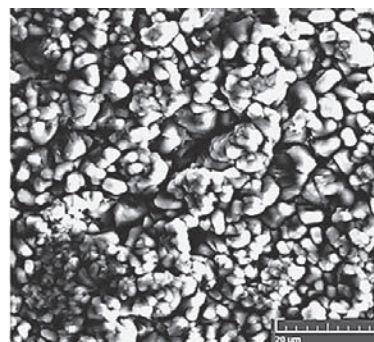


Figure 2 Scholzite coating on steel obtained from zinc - calcium phosphate bath

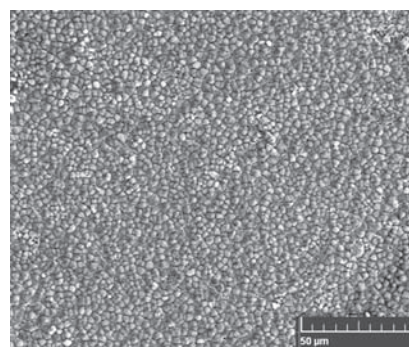


Figure 3 Phosphophyllite coating obtained from tri-cation ("three-cations") bath

were used: baths yielding thick zinc phosphate (Zn - Ph) Figure 1; zinc - calcium phosphate (Zn - Ca - Ph) Figure 2; phosphate formed by phosphophyllite only and deposited from the so-called tri-cation phosphating Figure 3; and bath yielding manganese phosphate (Mn - Ph) Figure 4.

Prior to the manganese and zinc phosphating, crystallization surface activation was performed using titanium polyphosphate that ensures formation of a fine crystalline structure. After degreasing, activation acid etching and phosphating, two - step rinsing (dip and spray) with demineralised water followed and drying in flowing air was applied.

RESULTS AND DISCUSION

Figure 5 shows DTA curves obtained by slow heating of smears of coatings deposited using commercial baths.

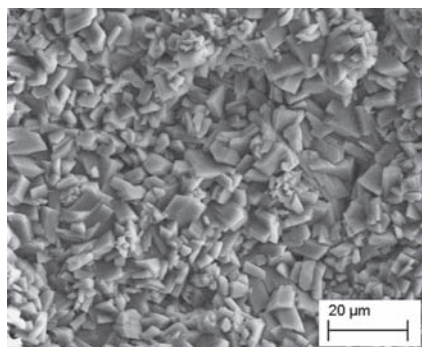


Figure 4 Hureaulite coating obtained from manganese phosphate bath

The dotted curve Zn - Ph shows the process of thermal loading of a thick zinc phosphate $Zn_3(PO_4)_2 \cdot 4H_2O$ coating. There is an evident endothermic peak that occurs at approximately 110 °C and disappears at approximately 180 °C. This endothermic peak has a minimum at 150 °C. A clearly visible convex arch of the curve (i.e. endothermic peak) is probably caused by the partial dehydration of hopeite. The curve then continues by smaller concave peaks at approximately 230 °C and 260 °C. The cause of these exothermic peaks (especially the one at 260 °C which, most probably, is not caused by analytical noise) is unknown. Another local endothermic area may be observed at temperatures ranging between 280 °C and 320 °C. This endothermic peak is a cause of eventual hopeite dehydration.

The dashed curve Zn - Ca - Ph shows the process of thermal loading of a zinc - calcium phosphate $Zn_2Ca(PO_4)_2 \cdot 2H_2O$ coating. Global endothermic peak may again be observed at temperatures ranging between 110 °C and 180 °C, but the decrease in temperature is smaller compared to the hopeitic coating. The reason of this endothermic reaction is probably scholzite dehydration. DTA curve of scholzite does not contain any convex peak up to 400 °C. However, a concave peak (endothermic reaction) may be observed at approximately 320 °C, its cause remaining unknown.

A curve formed by circles in Figure 5 and a full line in Figure 6 describes the behaviour of a "three - cations" phosphate coating (with the structure of coating $Zn_2Fe(PO_4)_2 \cdot 4H_2O$). Again, the convex endothermic peak is observed at first. However, its heat is less distinct and, moreover, compared with the scholzite or hopeite curve, the peak is shifted towards slightly higher temperatures (approximately 130 °C - 170 °C). It can be assumed that this peak is connected with a partial dehydration of phosphophyllite. Another peak - exothermic - shows at 320 °C (similarly to the DTA curve of scholzite), its cause is unknown.

A curve formed by square in Figure 5 and a dot dash curve in Figure 6 Mn - Ph describes the behaviour of a manganese phosphate $(Mn,Fe)_5H_2(PO_4)_2 \cdot 4H_2O$ coating. Again, there is a convex endothermic peak shifted towards even higher temperatures, 150 °C - 230 °C. The dehydration of a hureaulitic coating continues with another endothermic peak in a temperature range between

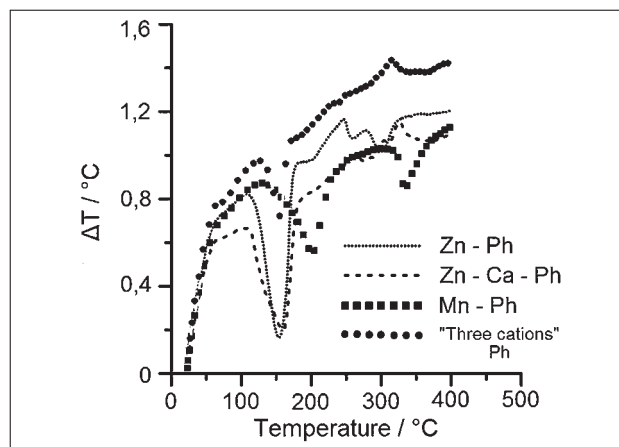


Figure 5 DTA curves of all examined phosphate coatings

320 °C and 360 °C. Figure 6 shows TGA curves obtained by slow heating of coatings deposited from the above mentioned commercial baths.

In the curve of thick zinc phosphate (Zn - Ph), a slow decrease in sample weight can be observed where temperature reaches 110 °C. The total weight loss in a temperature range between 110 °C and 150 °C is approximately 5 wt. %. Thus, it is clear that in such a temperature range the coating undergoes dehydration. Further heating causes further weight loss. At the temperature of 400 °C, the weight loss reaches approximately 12 wt. %.

In the curve of zinc-calcium phosphate (Zn - Ca - Ph), a steep decrease in weight of approximately 6 wt. % is discernible at approximately 100 °C - 150 °C. It is also caused by the coating dehydration. Weight loss is slightly steeper than in case of zinc phosphate and it reaches approx. 14 wt. %.

In the curve of tri-cation phosphate it can be seen that also in this case the sample undergoes dehydration in a temperature range between 110 °C and 170 °C. In this case the weight loss is approximately 10 wt. %. A total weight loss of this coating during heat loading up to 400 °C is approximately 14 wt. %.

A substantially different behaviour can be observed in the case of manganese phosphate, where a steep

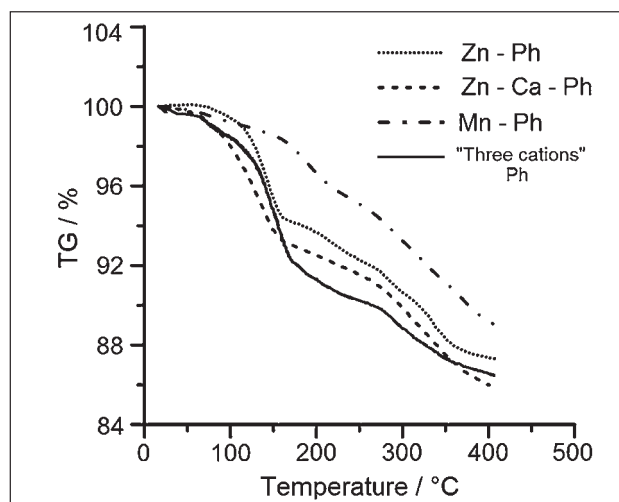


Figure 6 TG analysis of all examined phosphate coatings

weight loss can be observed in a temperature range between 170 °C and 230 °C. And the endothermic peak proves that at this temperature the coating undergoes dehydration. However, the weight loss reaches approx. 4 wt. %. Furthermore, from the character of the curve it can be deduced that the dehydration is slower than in case of other samples. The total weight loss after dehydration at 400 °C is approximately 10 wt. %.

During the gravimetric analysis the phosphate coated steel sheets were exposed to the temperature of 180 °C, which is clearly above the first dehydration step of all phosphate coatings. Results are shown in Figure 7.

The results declare the similarity in the dehydration of all phosphate coatings with the exception of manganese phosphate. Manganese phosphate at the selected temperature dehydrates only partially, which is in accordance with obtained DTA and TG curves.

The measured results of the dehydration of thick zinc phosphate are in good accordance with the results of other authors [1, 6]. Although these works state the temperature of the primal dehydration (leading to the formation of dehydrate) to be slightly higher, approximately 115 °C, and the temperature range of the final dehydration to be slightly higher as well, i.e. 300 -310 °C, even these authors did not observe exothermic peaks in the DTA curve of hopeite.

All the results obtained during experiments on a hureulitic coating in air are in good accordance with the results stated in [4]. It is thus proven that this coating undergoes a two-step dehydration process first at temperature between 150 and 230 °C and second at temperature between 320 °C and 360 °C.

CONCLUSIONS

The results shown in this work prove higher resistance of the manganese phosphate deposited on steel against thermal dehydration in normal atmospheric conditions. As this coating can be produced on steel in a thick form and because its structure shows the highest hardness, it can be readily used for the coating of parts subjected to intensive friction even with shorter period of intensive lubrication.

The resistance of other phosphate coatings against dehydration is the same, taking into account the exposition weight of samples. It is generally lower than that of the manganese phosphate. Expected higher resistance of phosphate coating produced by the modern tri-cation method was not observed. Moreover, the resistance of this type of coating is even slightly lower than in the case of traditional zinc phosphate coatings. The influence of crystal water in the coating on its dehydration behaviour has not been observed up to now. Scholzite coating (Zn - Ca - Ph) thermally dehydrates in a similar way as hopeite coating (Zn - Ph), although scholzite has two water molecules less than hopeite in its crystal structure.

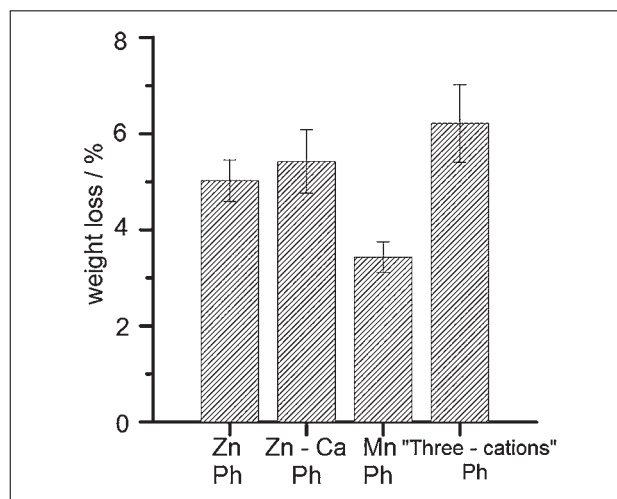


Figure 7 Phosphate coatings weight loss after thermal treatment at 180 °C

The dehydration of zinc-calcium phosphate and the dehydration of the coating produced by the tri-cationic process has not yet been studied and described up to now. The logical assumption that the thermal stability of zinc-calcium phosphate would be higher because of lower water content in the scholzite structure was not confirmed in this work. Neither was confirmed the suitability of coating produced by the tri-cation method. For the subsequent high-temperature processing, i.e. during the application of paint with high setting temperature or during the application of plasma-deposited ceramic coatings, the use of manganese phosphate with hureulite structure seems to be favourable.

Acknowledgments

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Note: The responsible translator for the English language is M. Jarkovska, CULS Prague, Czech Republic