

Phosphating of zinc surfaces in zinc-calcium solutions

D.I. Ivanova, L.B. Fachikov*

University of Chemical Technology and Metallurgy, 8 Kl. Ohridski Blvd, 1756 Sofia, Bulgaria

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This paper exhibits the results, obtained during the examination of the effect of calcium modified zinc phosphating compound on the processes of phosphate film formation on zinc surfaces. By means of gravimetric, chemical, electrochemical, and physical methods the characteristics of the compounds (density, pH, conductivity, total and free acidity) and of the produced coatings (thickness, phase and chemical composition, structure, protective capability) are determined.

It is found that with the increase of the working solution concentrations (5–15 %vol.), the thickness of the phosphate films increases, expressed stronger for the KAF-90 ZK compound; the medium temperature (20, 40, and 60°C) strongly affects the phosphate coating thickness for both phosphating compounds. The coatings, formed at 20°C, have the greatest thickness while the coatings, formed are at 60°C, the thinnest. The phosphate coatings consist of a single phase, the hopeite, and contain mainly the elements of Zn, P, O, a smaller quantity of Ni and traces of Ca for the coatings, produced in KAF-90 ZK solutions. The crystals nucleate from one center and grow spherulite-like. The phosphate coatings have high resistance in 3.5% NaCl. Those, produced in the calcium modified compound, exceed the ones produced in zinc-phosphate solutions.

Key words: zinc coatings, phosphating, carbon steels.

1. INTRODUCTION

During the past years, the production of zinc coated sheet steels with a lacquer-paint, laid on the surface, and polymer coatings, has considerably expanded. The most important indicator which determines the quality of such coatings is their adhesion to the metal surface. Because the adhesion of these coatings to metal has a physical and mechanical nature, the significance characteristics are the roughness and the surface tension. Therefore, the best preparation before laying organic coatings is to phosphate in such way that will increase 3–4 times the surface roughness and the surface tension. It provides good adhesion to zinc even for materials possessing high surface tension such as the polyethylene, polypropylene, and some others [1–4, 5].

The formation of a phosphate coating is a result of complex corrosion processes and of crystal nucleation and growth, running on the zinc surface. Their speed and interaction determine the crystallization kinetics, the structure and properties of the coating [3].

Compared to Cr^{6+} - passivation, phosphating improves the zinc resistance several times [1–3].

The phosphate films are considerably more resistant than the chromate at high temperatures. They ease the deep drawing, stamping, and rolling [4].

Optimum corrosion protection is achieved by phosphating and subsequent painting [3, 7].

The effect of phosphating Zn–Fe alloy coatings on the corrosion resistance is studied in [6]. It is found that the crystal phosphating shows much higher protection in comparison with the amorphous.

This paper presents the results, obtained during examination of the effect of calcium modified zinc phosphating compound on the processes of producing phosphate films on zinc surfaces. Determined are the density, pH, conductivity, and total and free acidity of the phosphating compound. The effect of the phosphating solution concentration and the temperature on the thickness of the formed coatings, their phase and chemical composition, is studied and their structure is characterized.

2. EXPERIMENTAL

Materials and samples

The specimens have the shape of disk (0.001 m²) and are made of mild steel sheet (0.17 % C) with thickness of 1.0 mm. The specimens are zinc-

* To whom all correspondence should be sent:

E-mail: : fachikov@uctm.edu

coated in chloride electrolyte, and the zinc coating thickness is approximately of 12 μm .

The preparation of the specimens prior to the tests covers in succession the following operations: alkaline cleaning, washing, etching, washing, and drying.

Solutions

The working media are water solutions of the KAF-101 ZT zinc compound as well as of its modified alternative of KAF-90 ZK, where 10 % of the zinc phosphate is replaced by calcium phosphate, and for which the ratio of $\text{P}_2\text{O}_5 : \text{NO}_3^- = 1:3$ is valid. The working conditions are as follows:

- concentrations: 5.0; 10.0; 15.0 % vol.
- temperatures: 20.0; 40.0; 60.0 °C.
- experiment duration: 5.0; 10.0; 15.0 min.

Methods of investigation

The gravimetric method. This method is used for investigation of phosphate coating formation kinetics in dependence of the effects of various factors. Its essence, it consists of determination of the specimen mass prior to phosphating m_1 , upon formation of the coating m_2 , followed by its removal, m_3 , measured in grams. By the values of m_1 , m_2 , and m_3 , the mass is calculated or to name it as it is accepted: M_1 is the phosphate coating thickness, M_2 is the dissolved substrate metal quantity, and M_3 is the change of the specimen mass during phosphating [9, 10].

The X-Ray structural method. It is used for determination of the phosphate coating phase composition. The investigations are performed using the TUR-M-62 apparatus with source $\text{CuK}\alpha$ 600/1°C.

EDX. INCA Energy 350 System, Oxford Instruments made, is used.

SEM. The analyses are carried out using the JEOL JSM 6390 microscope.

The electrochemical method. Using PAR – 263A the change of the potential with time is measured by exposure of the phosphatized specimens in 3.5 % NaCl.

The preparation of the specimens, the equipment used the investigations, and the methods of work are described in details earlier [9, 10].

3. RESULTS AND DISCUSSION

Characteristics of the phosphating solutions

Table 1 presents the values of the most important parameters such as the density, ρ ; pH;

conductivity, σ ; total (K_o) and free (K_c) acidity, which characterize the phosphating compounds. The data, given in the Table 1, exhibit that the densities of the both compounds are very close in value. However, the calcium modified phosphating compound has lower conductivity, higher pH, and possesses significantly lower total and free acidity.

Table 1. Characteristics of the phosphating compounds

Characteristic, compound	ρ , g/cm^3	pH	σ , mS/cm	K_o	K_c
KAF-90 ZK	1.330	1.08	163.7	280	32
KAF-101 ZT	1.335	1.00	168.7	320	40

Gravimetric studies

These investigations determined the effect of the working solution concentration, the temperature, and the duration of the phosphating process on the thickness/mass of the produced coatings (M_1), the quantity of the dissolved substrate metal (M_2), and the change of the specimen masses (M_3).

The parameters of concentrations (5, 10 and 15 % vol.) and temperatures (20, 40, 60 °C) are defined experimentally, criteria for their selection being the production of a uniform and dense phosphate film on the surface of the zinc coated specimens as well as the stability of the working solutions.

Figures 1 and 2 show the typical correlations of 'thickness/mass of the coatings – time', obtained at different concentrations and temperatures of the working solutions. It follows from the movement of the curves, in regards to the both examined phosphating solutions, that coating of greatest thickness is formed at the shortest time of specimen exposure to the working medium, i.e. 5 min. In case of a longer stay, the phosphate film mass/ thickness decreases or retains comparatively constant. All this shows that the phosphate coatings on the zinc surface form quickly (up to 5 min) after which their reorganization follows: interaction (exchange) with the components in the solution, resulting in compaction of the coatings and decrease in their mass. An exception of the observed regularity is the change of the specimens, obtained at 20°C, for all the examined concentrations of the KAF-90 ZK product. That is probably related to the known in the literature effect of the calcium ions on the crystal nucleation and growth during phosphating in zinc compounds, particularly at low solution temperatures [1, 4].

Fig. 1 and 2 show that with the increase of solution concentration, the phosphate film thickness

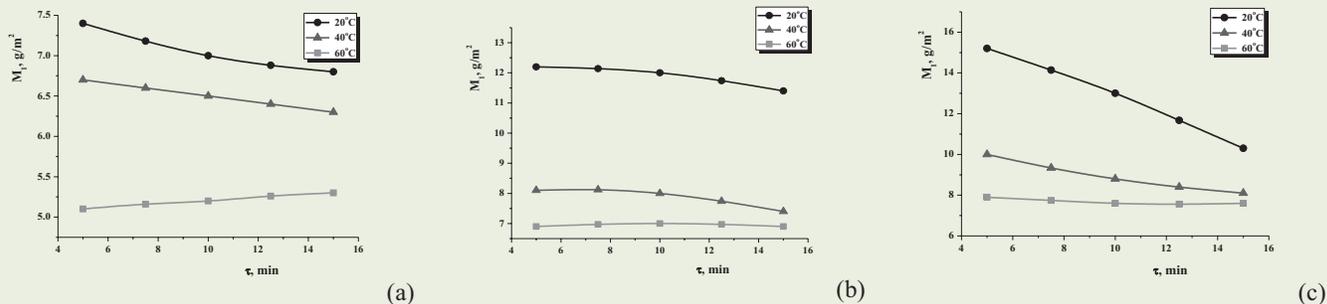


Fig. 1. Effect of the phosphating time, τ on the thickness/ mass of the produced phosphate coating, M_1 : a – 5 %; b – 10 %; c – 15 % (vol). (KAF-101 ZT)

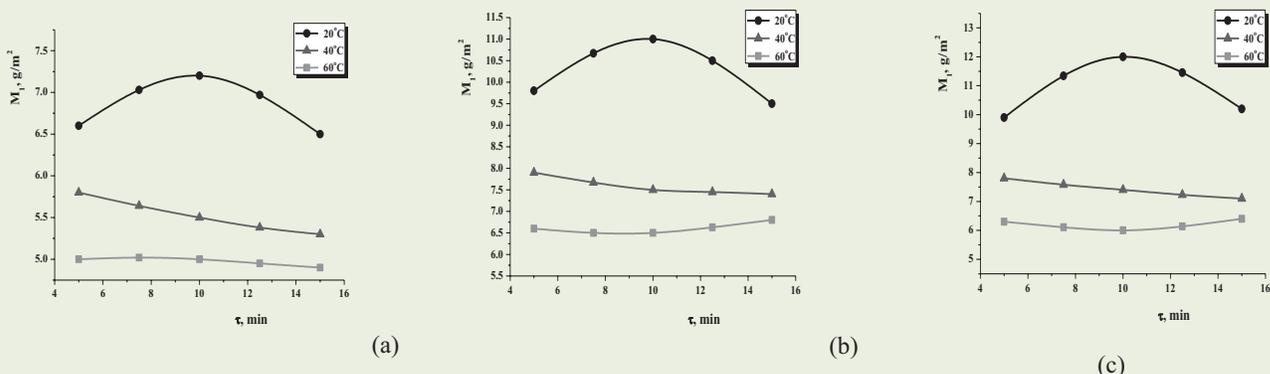


Fig. 2. Effect of the phosphating time, τ on the thickness/ mass of the produced phosphate coating, M_1 : a – 5 %; b – 10 %; c – 15 %vol. (KAF-90 ZK)

grows in both phosphating solutions, being the greatest at 20°C, and the smallest at 60°C. The presence of calcium ions (KAF-90 ZK) in the phosphating solution leads to the formation of thinner coatings, compared to those, formed in the pure zinc phosphating bath.

The visual observation (x 10) of the phosphatized zinc surfaces shows that with the temperature increase the uniformity and density of the coatings, formed in both phosphating solutions, increase.

The measurement of the mass (M_2) of the dissolved substrate metal (Zn) in the process of phosphate coating production shows that this mass increases with the time and with increase in the working solution concentrations, which should be expected from the phosphating process mechanism. Besides the close values of M_2 , obtained in zinc surface phosphating, it is also found that M_2 decreases with the temperature increase in both phosphating baths under other similar conditions. The above observation is an indication for a faster and more economical formation of phosphate films by increasing the temperature of the working solutions.

X-ray phase analysis

The results of the X-ray phase analysis, unless KAF-90 ZK is calcium modified, show the presence only of *Hopeite*, $(Zn_3(PO_4)_2 \cdot 4H_2O)$ and *zinc* in the formed phosphate coatings.

EDX – analysis

The EDX-analysis is performed on phosphatized specimens for both phosphating products at 60°C, in 15%vol. solutions, for 10 minutes (Fig. 3 and Fig. 4).

Determined by this analysis, the basic elements, contained in the coatings are Zn, P, O, and smaller quantity of Ni. The latter is contained in the solutions as an accelerator. The Ca contents in the phosphate coatings, formed in the solutions of KAF-90 ZK, are in the limit of error.

Electron microscope examinations

Fig. 5 shows photomicrography (SEM) of the phosphate coatings, formed on zinc coated specimens in the product solutions: (a) KAF - 101 ZT, and (b) KAF – 90 ZK, at a concentration of 15 %vol, for 10 minutes, and a temperature of 60°C.

It follows from the figure that the habitus of the coatings is permanent. The crystals form out from a

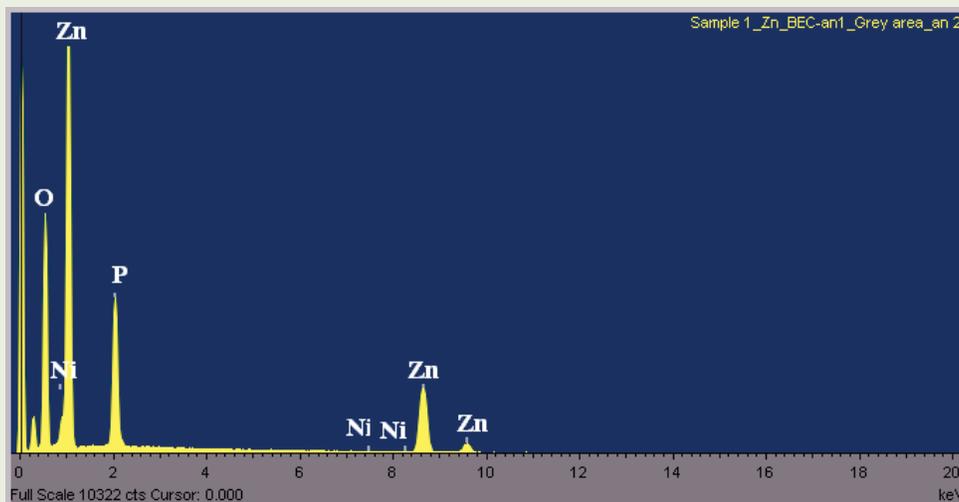


Fig.3. EDX – analysis of phosphate coatings formed in solutions of KAF-101 ZT.

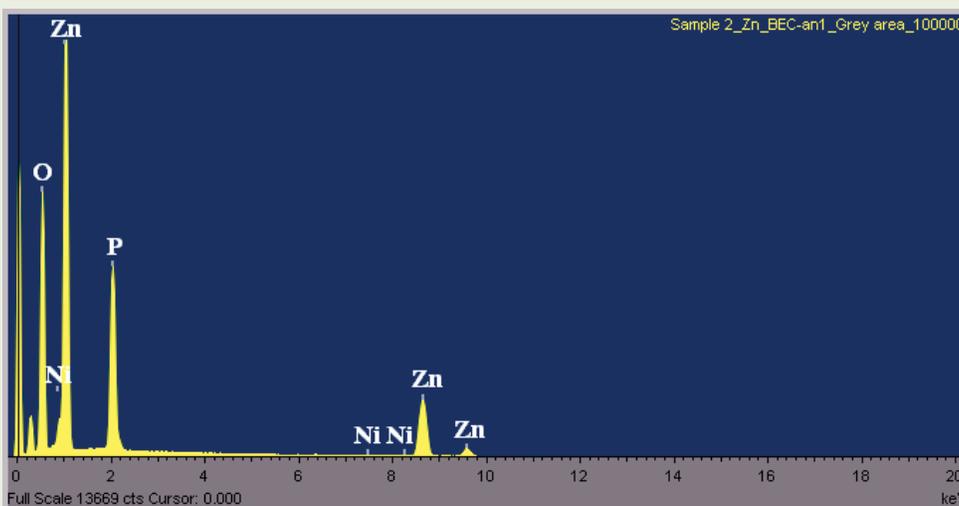


Fig.4. EDX – analysis of phosphate coatings formed in solutions of KAF-90 ZK.

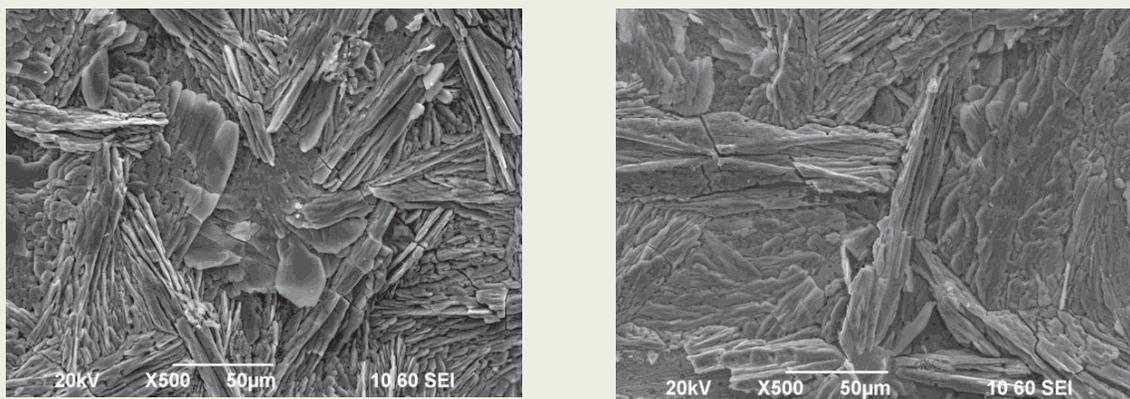


Fig. 5. Microphotography of phosphate coatings: a - KAF-101 ZT; b - KAF-90 ZK

single center and grow spherulite-like. Cracks are observed in the phosphate films of both

compounds. The crystal sizes are between 0.2 and 100 μm. The presence of more expressed and of

larger dimensions ‘leaf-like’ shapes of some of the crystallites, formed in the KAF-101ZT, could be pointed out as a more distinctive difference between the coatings.

Corrosion tests

The corrosion resistance, and the protective capability of the phosphate coatings, respectively (concentration of 15%vol., for 10 minutes at 60 °C), is determined in a 3.5% NaCl. The test is made by dipping the phosphatized specimens in NaCl. The coating is considered resistant and completely stable if there are no changes on the surface or coloring of the solution for two hours. This test also measures the corrosion potential of the specimens (Fig. 6) and the change of a non-phosphatized specimen potential is shown for a comparison.

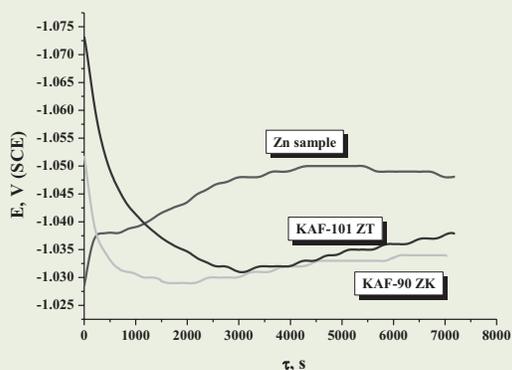


Fig.6. Dependence “potential, E – time, τ ”, during exposure of phosphatized specimens in 3.5% NaCl, 20±2°C.

The figure shows that the non-phosphatized specimen potential shifts to a negative direction, and becomes stationary after 50 min in a value of about –1050 mV (SCE). This evidences that the zinc surface activates in the working medium in the very beginning of the process.

The potentials of the phosphatized surfaces, produced in both of the phosphating products (KAF-101 ZT and KAF-90 ZK), shift sharply to a positive direction immediately upon dipping into the corrosion medium (expressed stronger for KAF-90 ZK), and they become practically equal after approximately 50 min for KAF-101 ZT, and 20 min for KAF-90 ZK. The shift of the potentials to a positive direction, most probably, is due to filling of the pores in the coatings with corrosion compounds.

4. CONCLUSIONS

The results, presented in this paper, suggest the following general conclusions:

- With increase of the concentration of the working solutions (5–15%vol.), the phosphate film thickness increases, expressed stronger for the KAF-90 ZK. Coatings of the greatest mass/thickness are formed within the shortest time of specimen exposure to the solutions, i.e. 5 min for all examined concentrations;

- The temperature of the medium (20, 40, and 60 °C) strongly affects the phosphate coating thickness for both phosphating products. The greatest thicknesses are formed at 20° C, and the thinnest at 60 °C.

- The mass of the phosphate coatings, produced in the both phosphating compounds, is greater in all specimen exposure times to the working solutions, than the mass of the dissolved zinc.

- The phosphate coatings consist of a hopeite single phase, and contain mainly the elements of Zn, P, O, smaller quantity of Ni, and traces of Ca, for the coatings formed in the solutions of KAF-90 ZK.

- The crystals nucleate from one center, and grow spherulite-like. The presence of more expressed and larger ‘leaf-like’ shapes of part of the crystallites, formed in the KAF-101 ZT, could be pointed out as a more important difference.

The phosphate coatings are of higher resistance to a 3.5% NaCl. Those, formed in the calcium modified product, have higher resistance than those produced in zinc-phosphate solutions.

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ФОСФАТИРАНЕ НА ЦИНКОВИ ПОВЪРХНОСТИ В ЦИНК-КАЛЦИЕВИ ПРЕПАРАТИ

Д. Иванова, Л. Фачиков

Химикотехнологичен и металургичен университет, 1756 София, бул. "Кл. Охридски" 8, България

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(Резюме)

В представената работа са показани резултатите, получени при изследване влиянието на модифициран с калций цинков фосфатиращ препарат, върху процесите на получаване на фосфатни филми върху цинкови повърхности. Посредством гравиметричен, химичен, електрохимични и физични методи са определени характеристиките на препаратите (плътност, рН, проводимост, обща и свободна киселинност) и на получаваните покрития (дебелина, фазов и химичен състав, структура, защитна способност).

Установено е, че с увеличаване на концентрацията (5-15%) на работните разтвори, дебелината на фосфатните филми нараства, по-силно изразено за препарата КАФ-90ЦК; температурата на средата (20, 40 и 60° С) оказва силно влияние върху дебелината на фосфатните покрития и за двата фосфатиращи препарата. С най-голяма дебелина са покритията получени при 20° С, а най-тънки - при 60° С; фосфатните покрития се състоят от една фаза: хопеит и съдържат главно елементите Zn, P, O, в по-малко количество Ni и следи от Ca, за покритията получени в разтвори на КАФ-90ЦК; кристалите се зараждат от един център и нарастват сферолитоподобно. Фосфатните покрития са с висока устойчивост в 3.5% NaCl като тези, получени в модифицирания с калций препарат, превъзхождат получените в цинково-фосфатните разтвори .