

ZINC-MANGANESE PHOSPHATING OF CARBON STEELS: CHARACTERISTICS OF SOLUTIONS AND COATINGS

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ABSTRACT

The characteristics of solutions (density, pH, conductivity, total and free acidity) as well as of coatings (thickness, phase and chemical composition, structure, protective ability) in phosphating of carbon steels in concentrates, containing zinc and manganese phosphates in different ratio (9:1, 7:3, 5:5 and 3:7) have been determined by gravimetric and analytical methods and electron microscopic, X-ray and ICP analyses.

It has been established that by increasing the content of manganese phosphates in concentrates, their density, pH and total acidity decrease, free acidity increases and their conductivity retains comparatively equal. At the same time the thickness of the coatings obtained at all studied temperatures (60-90°C) and the quantity of the dissolved metal of the substrate increase in the same conditions. The phosphate coatings consist mainly of the following phases: hopeite, phosphophillite, and hureaulite. Their habitus retains as the size of grains decrease by increasing the content of manganese phosphates in solutions.

The phosphate coatings have high corrosion resistance in 3.5 % aqueous solutions of sodium chloride and their corrosion potential is displaced in positive direction by increasing manganese phosphates.

Keywords: zinc-manganese phosphating, carbon steel, coatings, phase composition, properties.

INTRODUCTION

Phosphating of metals refers to the so-called conversion processes in which as a result of complex physicochemical reactions, transformations of metal substrate in new surfaces possessing non-metallic and electrical insulating properties are performed [1-4]. The application of phosphating, created originally for protection against corrosion was expanded significantly including its application as a sub-layer before laying on lacquer-paint and polymeric coatings, as hard lubricants in wire drawing and cold deformation of metals, for obtaining wear resistant and electro insulating coatings, etc.

The energy rise in price of worldwide importance increased the interest in creating low temperature phosphating processes including manganese (through zinc modification, nitric acceleration, etc.), to work at low temperatures and to retain their high qualities [2].

This study continues the experiments on phosphating of iron-carbon alloys in solutions containing zinc and manganese phosphates in different proportions [5, 6].

EXPERIMENTAL

Materials and solutions

The experiments were carried out with samples of low-carbon steels, st.3 (0.17 % C). The sample shapes

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under gravimetric tests were square (0.005 m²) and for SEM and X-ray experiments - a disk with area of 0.001 m².

The preparation of work samples included operations as: alkaline degreasing, water rinsing, pickling, water rinsing and drying with filter paper.

Aqueous solutions of the concentrates KAF-90 ZM, KAF-70 ZM, KAF-50 ZM and KAF-30 ZM, containing zinc and manganese phosphates at a ratio of 9:1, 7:3, 5:5 and 3:7 were used as working media for phosphating.

The experimental conditions were:

- concentrations: 10.0; 15.0; 20.0 vol.%
- temperatures: 60.0; 70.0; 80.0; 90.0°C
- duration of the experiment: 0.5; 1.0; 3.0; 5.0; 10.0; 15.0; 20.0 min.

Methods

Gravimetric method. This method was used for studying the kinetics of forming phosphate coatings and establishing the regularities of processes, depending on the influence of different factors. The gravimetric method determines the alteration of the samples before phosphating m_1 , after obtaining the coating m_2 and after its removal m_3 , in grams. The following formulas were used:

$$M_1 = \frac{m_2 - m_3}{S}, \text{ g/m}^2$$

$$M_2 = \frac{m_1 - m_3}{S}, \text{ g/m}^2$$

$$M_3 = \frac{m_2 - m_1}{S}, \text{ g/m}^2, \quad \text{where}$$

M_1 is phosphate coating mass; M_2 - dissolved mass of metal substrate; M_3 - alteration of the sample mass under phosphating; S - sample surface area, m².

Electron microscopy. This method was used for determining the structure of phosphate coatings obtained - roughness or micro geometry of their surface. Analyses were carried out by a SEM - JEOL JSM 35 CF.

X-ray method. The X-ray structural analysis was used for determining the phase composition of phosphate coatings. The experiments were carried out by apparatus TUR - M - 62 with a source Cu, Ka, 600/1.

ICP. It was used for the analysis of main elements

and impurities in coatings. The analysis was carried out by Vista MPX apparatus.

Some water was added to the weighed volume of the phosphate concentrate at room temperature. It was kept at a certain temperature and the pre-weighed samples were dipped into the solution. After a determined time interval of treatment, the samples were removed, rinsed with water, dried with filter paper and weighed (m_2). Then the coating was removed in inhibited hydrochloric acid and weighed.

M_1 , M_2 , and M_3 were calculated by the values obtained for m_1 , m_2 , and m_3 .

RESULTS AND DISCUSSION

Four concentrates containing phosphates of Zn and Mn at a ratio of 9:1, 7:3, 5:5, and 3:7 have been studied. These concentrates as mixtures of mono-substituted phosphates of Zn and Mn contained accelerators, stabilizers and other agents ($P_2O_5:NO_3^- = 1:3$). Table 1 presents values of the most important characteristics: density, ρ ; pH; conductivity, σ : total K_o and free K_c acidity. The data presented in Table 1, show that by increasing the content of manganese phosphates in the concentrate its density decreases insignificantly, pH becomes lower more than two times and its conductivity remains comparatively equal. Total acidity increases and free acidity decreases.

The concentrations (10-20 %) and temperatures (60-90°C) of the solutions were determined experimentally. A criterion for their selection was the obtaining of a thick even phosphate film on the sample surface and the stability of the working media.

Fig. 1 presents the kinetic dependence "phosphate coating mass - time" obtained at different temperatures of the phosphate solutions. It can be seen that the coating mass is maximal at about the fifth minute from the beginning of the process, as this time increases by enrichment

Table 1. Characteristics of concentrates.

№	characteristic, concentrate	ρ , g/cm ³	pH	σ , mS/cm	K_o	K_c
1	KAF-90 ZM	1.340	0.39	188.9	376	67
2	KAF-70 ZM	1.323	0.37	182.0	357	77
3	KAF-50 ZM	1.32	0.25	183.1	342	85
4	KAF-30 ZM	1.312	0.17	184.6	340	90

of manganese phosphates in the solution. Then the values of M_1 gradually decrease probably due to the restructuring and compacting of coatings as a result of the exchange of phosphates both in the film and in the solution.

Fig. 1 shows also that the thickest coatings are obtained in solutions with high content of zinc phosphates (KAF-90 ZM), at all studied temperatures as with its decrease, respectively increasing of manganese phosphate in the solution, the coatings became thinner.

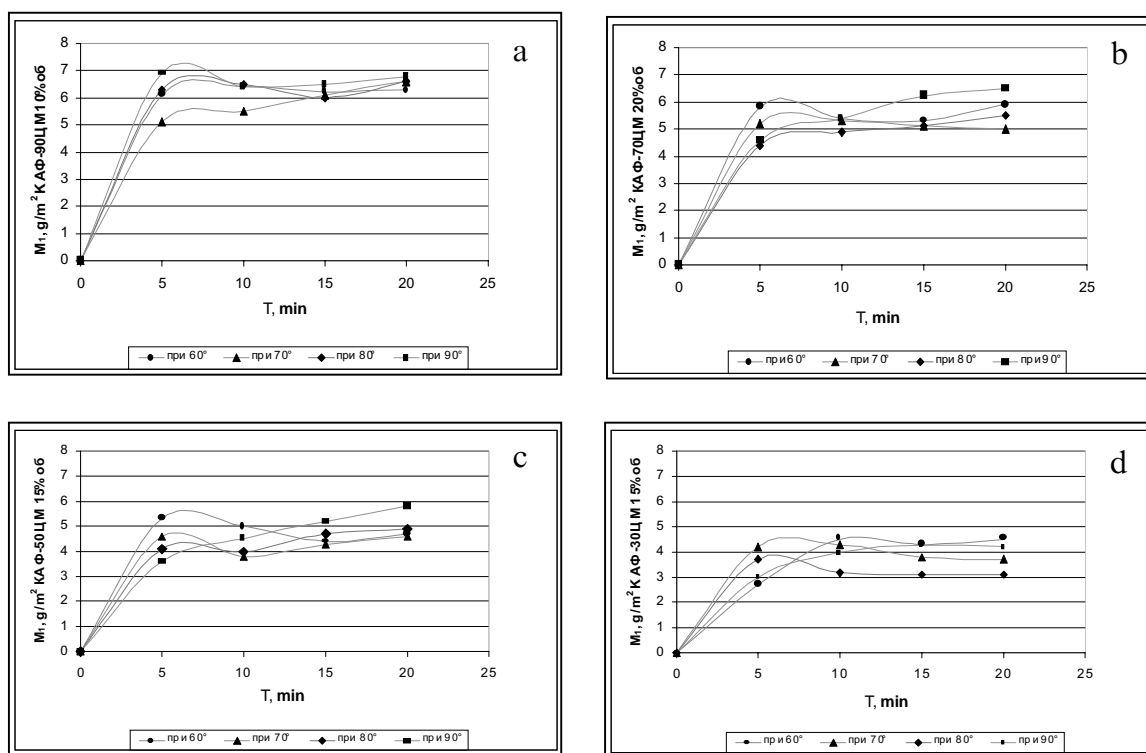


Fig. 1. Effect of the phosphating time τ on the thickness of the deposited coating, M_1 : a- KAF-90 ZM; b-KAF-70 ZM; c-KAF-50 ZM; d- KAF-30 ZM.

In addition, the increase in the content of manganese phosphates leads to an alteration of the temperature influence on the thickness of the forming films, while in KAF-90 ZM (with lowest content of manganese phosphate) by increasing the temperature the values of M_1 grow, but for the other phosphate concentrates this effect is reverse. All these regularities can be related to the different influence of the two phosphates on the processes of phosphate crystal formation and growth at the studied temperature interval.

As it can be expected from the phosphating mechanism, the dissolved metal mass of substrate, M_2 increases according to the time and the temperature of the working

solutions and it is better expressed by increasing the content of manganese phosphates. The latter can be related both to decrease in pH under these conditions and to lower rates of manganese formation in comparison with zinc phosphating.

Except phosphating in KAF-90 ZM, where until about the 10th minute interval, the mass M_1 of the coating obtained was bigger than the dissolved metal mass M_2 , the other phosphate concentrates demonstrated larger quantity of the dissolved metal at all temperatures.

Fig. 2 presents variations of M_1 , M_2 and M_3 values obtained in the same conditions and temperatures of different phosphate concentrates.

It is evident that phosphate coatings are formed comparatively quickly (Fig. 2, a), as a delay of this forming can be observed by increasing manganese phosphate in solutions. The coating thickness changes in the same way.

Curves M_2 - τ (Fig.2,b) demonstrate exactly the opposite tendency - the dissolved metal mass increases by decreasing zinc phosphate content in the medium.

Fig. 2 shows that, except the solutions of KAF-90 ZM under phosphating, the rest concentrates dem-

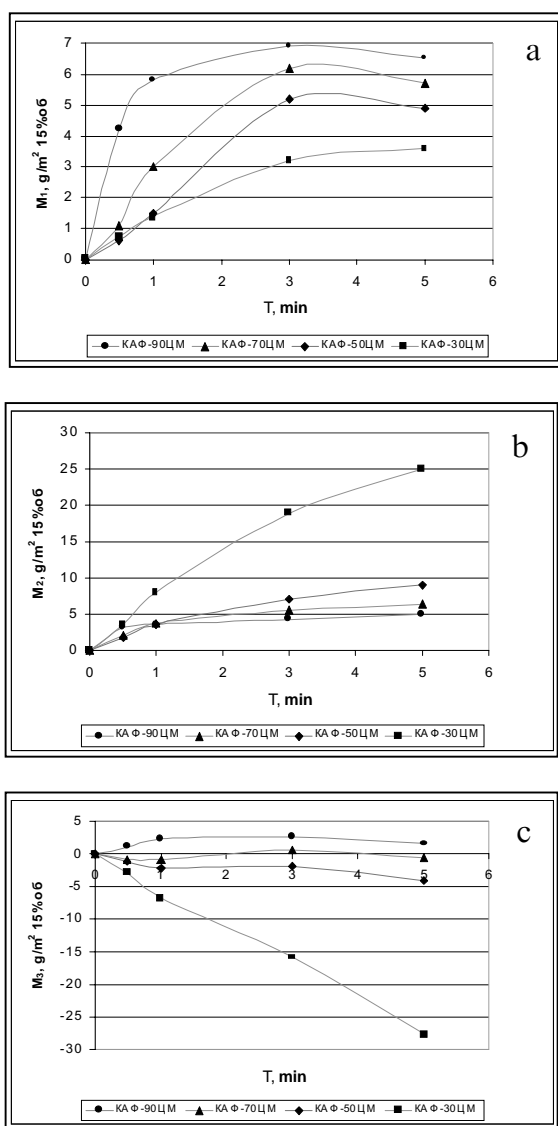
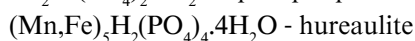
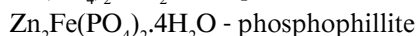


Fig. 2. Phosphating in solutions, 15% vol., 70°C: a- M_1 ; b- M_2 ; c- M_3

onstrate more dissolved metal than the mass of the phosphate coating.

X-ray analysis of the phosphate coating obtained, shows presence of the following phases.



The quantity correlation of the phases varies for different phosphate concentrates: hopeite predominates in

KAF-90 ZM, followed by phosphophillite in which Fe is partially substituted by Mn - $Zn_2(Fe,Mn)(PO_4)_2 \cdot 4H_2O$. By increasing the content of manganese phosphate the quantity of hopeite decreases in return for phosphophillite, but in KAF-50 ZM hureaulite is formed in a larger quantity.

Table 2 shows the manganese and zinc content of coatings that were obtained in 15 %, 70°C defined by ICP. The data in the Table 2 show that variation in Mn and Zn in the coatings has led to analogous content of their phosphates in the concentrates. For example, the quantity of Zn decreases about 4 times from KAF-90 ZM to KAF-30 ZM while Mn increases two times.

Fig. 3 shows microphotography (SEM) of the phosphate coatings, obtained on steel samples in solutions with concentration of 15%, temperature 70°C for 10 min.

It follows from the figure that the habitus of coatings is constant -crystals are formed only from one center. The alteration in the size of crystals, which decrease and compact by increasing the content of manganese phosphates, is evident.

The corrosion resistance, respectively protective capacity of phosphate coatings was determined in 3.5 % NaCl (GOST 9.302-86). During the tests the phosphate samples were dipped into solution of NaCl. The coating can be determined as stable if there is no alteration on its surface and color of solution for three hours. There were no changes established on the coatings, obtained in different phosphate concentrates for this time.

The corrosion potential, E (Fig. 4), was determined during the experiments and the alteration of a non-phosphate sample was shown for comparison. Fig. 4 shows that by increasing the content of manganese phosphates in concentrates, the corrosion potential becomes more positive that is an evidence for higher resistance of the coatings obtained in their solutions. After a 60 minute interval the potential of coatings, obtained in KAF-90 ZM, KAF-70 ZM and KAF-50 ZM blent and remained

Table 2. Mn and Zn content in phosphate coatings.

metal	KAF-90ZM	KAF-70ZM	KAF-50ZM	KAF-30ZM
Mn	0.90	0.96	1.33	1.80
Zn	25.70	9.28	8.23	6.58

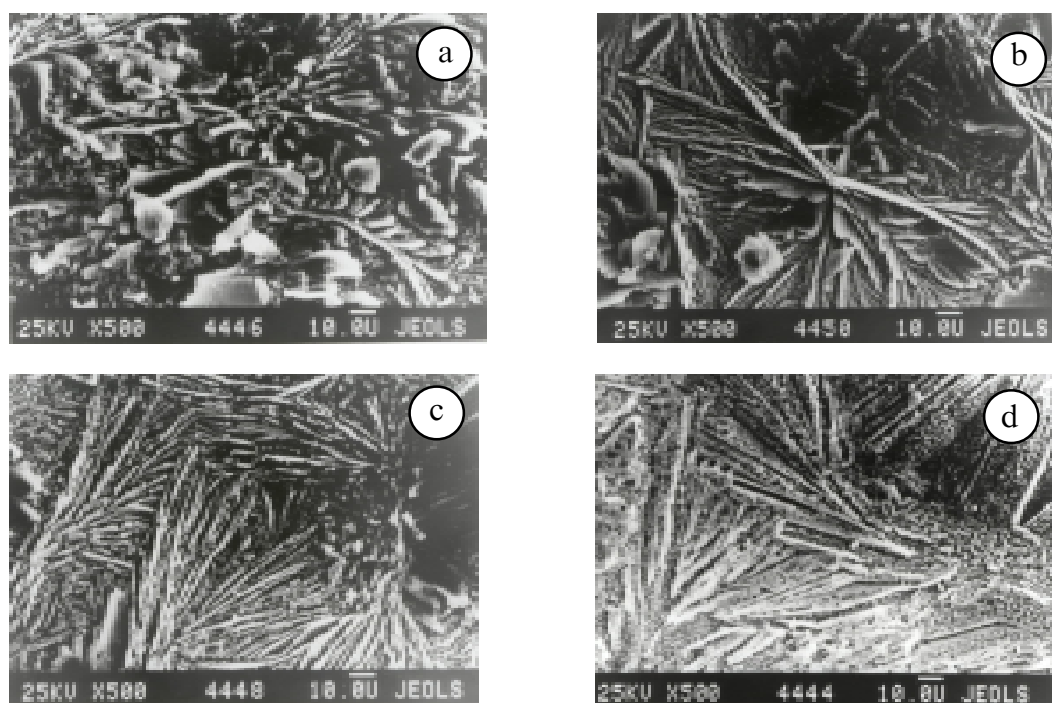


Fig. 3. SEM analyses of phosphating coatings: a-KAF-90 ZM; b-KAF-70 ZM; c-KAF-50 ZM; d-KAF-30 ZM.

constant - about 600 mV, SCE. The corrosion potential of the coating obtained in KAF-30 ZM is about 50 mV more positive. The corrosion potential of the non-phosphate sample is about 200 mV more negative than the corrosion potential of the coating obtained in KAF-30 ZM and about 130 mV for the rest.

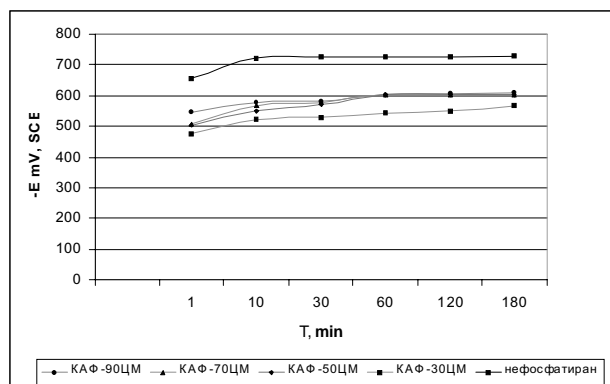


Fig. 4. Relationships E- τ , 3.5% NaCl.

CONCLUSIONS

It has been established from the tested concentrates containing zinc and manganese phosphates at different ratio that:

By increasing quantity of manganese phosphates, density, pH and total acidity of concentrates decrease, free acidity increases and their conductivity retains relatively constant;

By increasing manganese phosphates, the coating mass decreases and the amount of the dissolved metal of the substrate increases and the time to form the coatings increases;

The phosphate coatings consist mainly of the phases hopeite, phosphophillite and hureaulite, as their relation depends on the content of zinc and manganese phosphates in the concentrates;

The phosphate coatings possess high resistance in 3.5 % NaCl, as their corrosion potential is displaced to the positive direction at higher content of manganese phosphates.

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