



Amorphous Phosphate Coatings on Steel Surfaces – preparation and characterization

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Abstract Gravimetric and electrochemical methods, XRF, TEM, XPS, AFM and AES analyses have been used to determine the influence of concentration (2-10 vol.%), pH (2÷6), temperature (20÷80°C) and agitation (0÷2000 rev min⁻¹) of the solutions over the thickness, composition, structure and passivation characteristics of the phosphate coatings on low carbon steel surfaces.

Keywords: amorphous phosphating, iron phosphating, carbon steels.

1. Introduction

The phosphating process is used widely to produce compositional and microstructural changes in the surfaces of carbon steels by forming an inorganic, insulating thin coating. The ban on the using of chromate conversion coatings, has made the amorphous iron phosphating an important means for preliminary processing of steel surfaces. Phosphating with non-crystalline coatings, which are formed in low-acid solutions of alkaline and ammonium phosphates, have a number of advantages compared to crystalline coatings [1, 7]:

- cleaning and phosphating simultaneously;
- stability, long exploitation and easy control of the solutions;
- low working concentrations;
- low sludge formation;
- insignificant expense for waste water treatment;
- can act as a temporary corrosion protection film;
- very good adhesion to subsequent paint and polymer coatings.

The amorphous or light iron phosphate coatings are typical conversion coatings adhering to the metal surfaces. Depending on the composition of the phosphate bath the colour of the phosphate coating varies from light and dark grey to dark blue. Despite their high porosities and small thickness these coatings have been developed and widely applied during the past decades in order to enhance the adhesion and the protective characteristics of paint and polymeric surface coatings [2-6].

This study presents the author's investigation of the newly developed product KAF-09OF and concerns the preparation and characterisation of amorphous phosphate coatings on low carbon steels.

2. Experimental

2.1. Materials and samples

Sheet formed mild steel (0.17%C) with a thickness of 1.0 mm was used to prepare samples for testing. For the gravimetric test, the sample area was 0.005 m², for the polarisation experiments - 0.00005 m² and for the other physical testing methods, described below, 0.001 m².

The sample pretreatment includes operations such as alkaline degreasing, water rinsing, acid pickling, water rinsing and drying with filter paper.

2.2. Solutions

The working media are aqueous solutions of the preparation KAF-09OF with concentrations of 2.0, 5.0 and 10.0%, vol.; pH 2.0, 4.0 and 6.0 and temperatures of 20, 40, 60 and 80°C.

KAF-09OF is a liquid concentrate of ammonium and alkaline phosphates, stabilising additives – buffers, softeners, activators (both inorganic and organic), as well as surfactants – a non-ionic and an anionic detergents.

2.3. Methods

Gravimetric method

The mass M (g m⁻²) and thus the thickness of the coatings can be determined by the differences in the masses of the samples after forming m_1 ,g and removal of the coatings m_2 ,g, namely

$$M = (m_1 - m_2)/S$$

S is the sample area, m².

The reason for the adoption of coating mass rather than coating thickness as the usual measure of coatings is the difficulty in measuring the latter compounded by the uneven nature of the substrate and of the coating.

Potentiodynamic polarization method

The electrochemical investigations were carried out in a conventional three electrode cell with a platinum counter electrode and a saturated calomel reference electrode (SCE). The measurements were performed with a PAR-263A potentiostat and M352 Soft Corr Corrosion Measurement and Analysis Software. The rotation speed of the disc electrode was varied within the range 0–2000 rev min⁻¹ in order to obtain a set of anodic polarisation curves.

Measurement of electrode potentials

The potential value is important in the estimation of the nature of the electrode process. The experiments were performed with an automatic device PAR-263A.

X-ray fluorescence (XRF)

The method determines the composition and quantity of the elements present in the coatings, and was performed with equipment ED 200 (Oxford Instruments, UK).

X-ray photoelectron spectroscopy (XPS)

The chemical composition and the oxidation state of the elements on the surface being formed were studied using XPS. The XPS studies were performed in an VG ESCALAB II system with Al K α radiation with an energy of 1486.6 eV and total instrumental resolution of ~1 eV. The elemental concentrations were evaluated from the integrated peak areas after linear background subtraction using theoretical cross-sections.

TEM. This method was applied to investigate the structure of the phosphate coatings obtained using an EM-400 (Philips) instrument.

Auger analysis (AES)

The analysis determined content and distribution of the elements in the depth of the phosphate coatings. Riber's device LAS 3000 was used.

Atomic force microscopy (AFM)

Atomic force microscopy imaging was performed using the NanoScopeV system (Veeco Instruments Inc.) operating in tapping mode in air at room temperature. Silicon cantilevers (Tap300Al-G) with 30 nm thick aluminium reflex coating were used. The tip radius was <10 nm. The scan rate was set at 1 Hz. Images from three independent experiments were analysed.

3. Results and discussion

The effect of pH and the temperature of phosphating solutions with concentration of 5.0 vol.% (determined as the optimum) on the mass/ thickness of coatings M , was studied by gravimetric experiments. Each point used in the calculations was obtained as an arithmetic average of three experimental runs (tests of three samples). The plots in Fig. 1 are almost straight lines, meaning that the phosphate coating thickness grows with approximately constant or only slightly varying rate. Under these circumstances, the coatings obtained at pH 2.0 exhibit the greatest mass, on average twice as heavy as those obtained under pH 4.0 and 6.0. This effect can be attributed to the more aggressive aqueous solutions with pH 2.0 where probably large metal quantities participating in the specimen phosphating were dissolved.

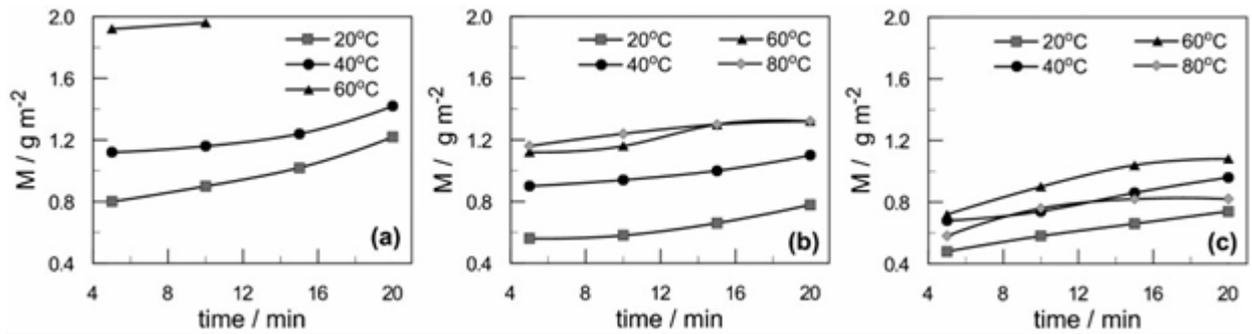


Figure 1. Relationships of mass/thickness versus time, for coatings obtained in 5 vol. % solution of KAF-09OF: a pH 2.0; b pH 4.0; c pH 6.0

The thickness of the coatings increases 2–3 times for all pH values of the solutions as the temperature of the bath increases from 20 up to 80°C (see Fig. 1). This effect can be associated with the high dissolution rate of the substrate as the temperature of the baths increases. The gravimetric experiments reveal that at pH 2.0 and solution temperature > 60 °C (and time to exposure >10 min), black powdered coatings were formed. These coatings exhibit weak adhesion to the metal surface and are impractical. The main outcome of these tests is that solutions with the lower pH values can be used for coatings at batch temperatures ranging from 20 to 40°C.

The results reveal that the best conditions for formation of amorphous phosphate coatings are: pH 4.0–4.5 and temperature of solutions 50–60 °C.

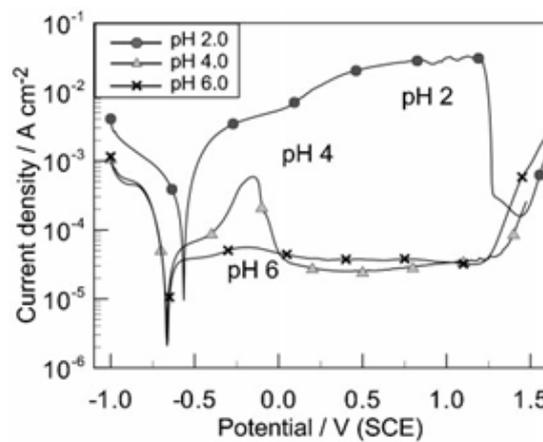


Figure 2. Polarisation curves at different pH of solutions, 5 vol. %, 20°C, 1 mV s⁻¹

The potentiodynamic polarisation relationships plotted in Fig. 2 were developed in solutions of 5.0 vol.% KAF-09OF and various pH values. The recordings were performed in a potential range from -1.0 to 1.6 V and a scanning rate of 1 mV s⁻¹. The course of the curves indicates that the potential at which the anode polarisation of the samples at pH 2.0 starts is with approximately 100 mV more negative than those determined in solutions with pH 4.0 and 6.0. This implies that the steel transition into a passive state is facilitated under pH 2.0 of the solution, confirmed by the higher current values at this potential. The plots in Fig. 2 reveal that a typical curve of anode passivity of steel (in 5 vol.% solution of KAF-09OF) is

observed only at pH 4.0, while at pH 6.0 immediate transition into a passive state occurs. Probably, at pH 2.0, salt coatings form on the sample surfaces which requires potentials beyond 1250 mV(SCE) to passivate the steel.

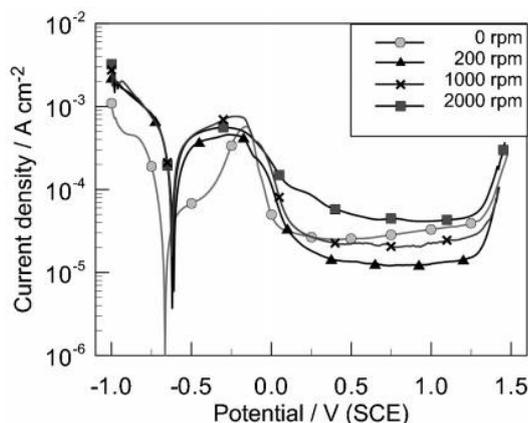


Figure 3. Polarisation curves for various rotation speeds (0–2000 rev min⁻¹), 5 vol.%, 20°C, pH 4.0, 1 mV s⁻¹

The effect of the stirrer agitation rate (0–2000 rev min⁻¹) on the polarisation relationships E–log*i* is shown in Fig.3, where the potential range varies from -1.0 to 1.6V with a scan rate of 1.0 mV s⁻¹. When the agitation speed increases, the potential for anode polarisation shifts slightly towards the positive direction with increasing current. The effects of the agitation intensity are most probably related to enhanced cathode reaction as a result of improved supply of the depolariser (the dissolved oxygen in the medium, for example) to the metal surface that improves the formation and increases the stability of the passivation film.

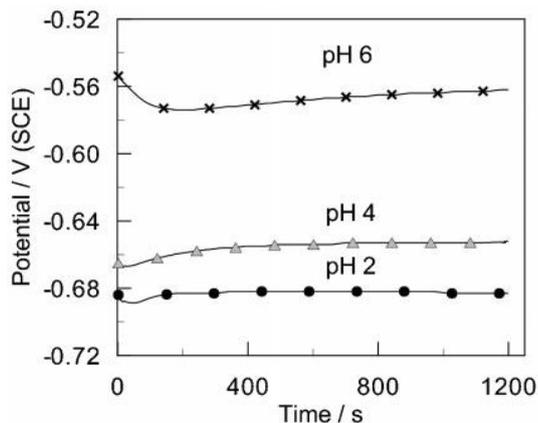


Figure 4. Open circuit potential versus time in solutions of 5 vol. %, at 20°C

The time variations of the electrode potential (Fig.4) during the phosphate coating formations indicate slight shifts of the potentials towards more negative values (for all values of pH of the solutions). The latter is related to the activation (dissolution) of the metal surface. Then, as a result of the formation of both the oxide and the phosphate films, the potentials alter towards more positive values. With increase in the pH, the potential at which the phosphate coating forms, shifts towards more positive values; at pH 6, for instance, this is ~100 mV higher.

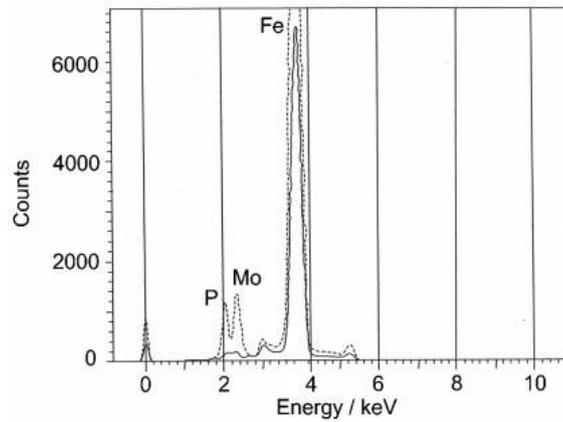


Figure 5. X-ray fluorescence analysis of metal surface without phosphate coating (thick line) and with it (dotted line): coating conditions 5 vol.%, pH4.0, 60°C, 5 min

The X-ray fluorescence analysis data in Fig.5 (the thick line corresponds to the clean metal surface, while the dotted one refers to post-coating) indicate that the elements P and Mo are missing (or in negligible quantity) on the clean surface, while in the coating, their quantities increase significantly. The increase in the iron content indicates that Fe^{2+} ions (in consequence of substrate dissolution) are transformed into oxides and phosphates, i.e. as components of the coating.

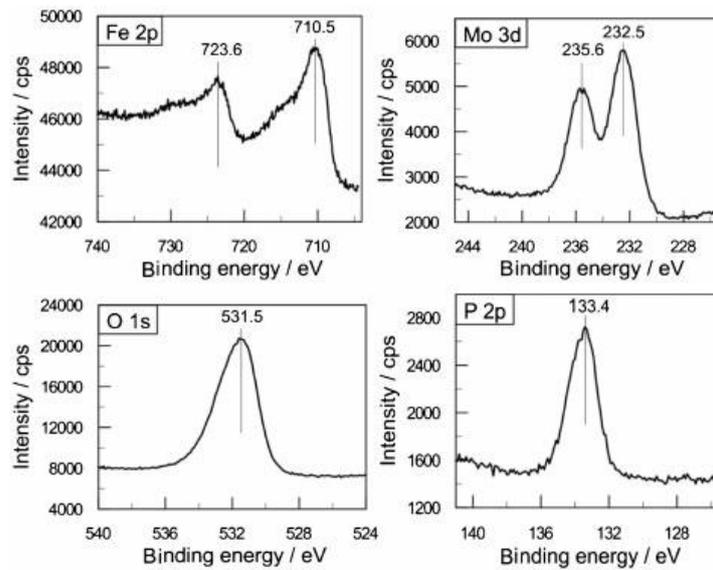


Figure 6. X-ray photoelectron spectroscopy analysis of coating obtained in 5 vol.% solution, pH 4.0, 60°C, 5 min

The composition and concentration of the basic elements of the coating – O, P, Fe and Mo – were determined by XPS (Fig. 6 and Table 1). The compounds formed by them are most probably oxides and phosphates of Fe and Mo.

Table 1. Concentration of elements in coating determined by XPS/at.%

O, at %	Mo, at %	P, at %	Fe, at %
58.97	6.71	9.35	11.50

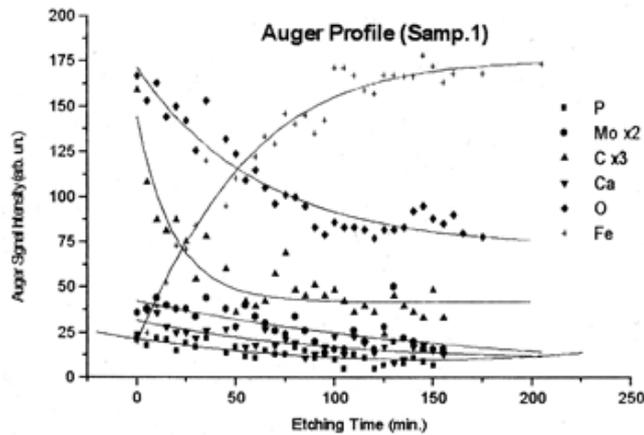


Figure 7. AES of a phosphate coating obtained in 5 vol. % solution, pH 4.0, 60°C, 5 min

The Auger spectrogram demonstrates the results obtained with a simple in 5 vol. % solution of KAF-09OF at 60°C. The analysis of the spectrogram gives elements forming the coating (Table 2). The data summarized show that element concentrations decrease with the depth of the coating and this effect is strongest with respect to C and O₂ (well known as air absorbents). Only amount of Fe increases which is typical for that type of coating.

Table 2. Content of elements(at.%), determined by AES profile

Element	5min	35min	155min
C	23.9	11.5	5.6
O	39.0	26.1	17.6
P	4.1	3.2	1.1
Ca	9.8	4.5	3.1
Fe	16.2	49.4	69.0
Mo	7.0	5.4	3.6

The TEM image of the steel surface (Fig.8a and b) performed by the two step replicas method indicates that the surface structures are heterogeneous. The surface without coating (Fig.8a) is of weak expressed relief: there the amorphous coatings cover the steel surfaces with undefined profile and strongly expressed relief (Fig.8b).

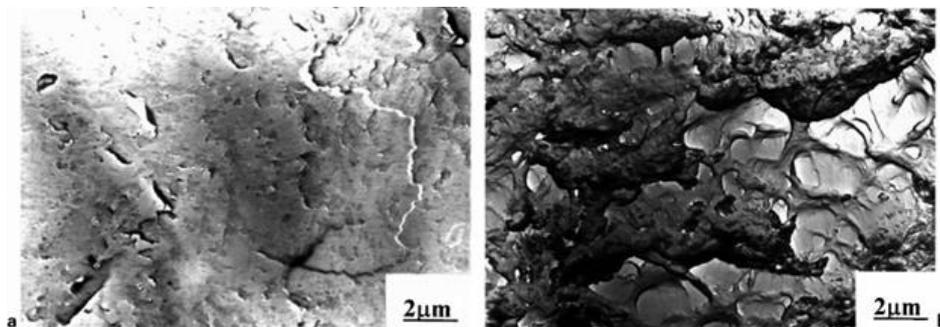


Figure 8. Image (TEM): a - before and b - after obtaining phosphate coating, 5 vol.%, pH 4.0, 60°C, 5 min

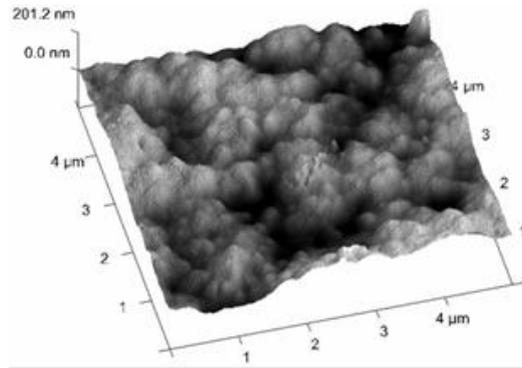


Figure 9. Atomic force microscopy spectrum of phosphate coating, 5 vol.%, pH 4.0, 60°C, 5 min

The roughness of the amorphous phosphate coatings was determined through AFM (Fig.9 and Table 3). The roughness average value of the coatings obtained in the phosphating solution under the circumstances imposed (5.0 vol.% KAF-09OF and pH 4.0 at 60°C) was estimated at about $S_a=805.6$ nm. The well developed surface roughnesses of the phosphate coatings, as well as their chemical contents, enhance the adhesion to subsequent paint and polymer coatings.

Table 2. Content of elements (at.%), determined by AES profile

Surface area, μm^2	R_q , nm	R_a , nm	R_{max} , nm	R_p , nm	R_v , nm
25.7	33.4	26.7	237	153	-84

4. Conclusion

The influence of pH, temperature and agitation on the kinetics of formation, composition and characteristics of the coatings obtained in solutions of the newly developed process KAF-09OF has been investigated by gravimetric, potentiodynamic polarisation and physical methods. It has been established that the coatings develop the highest mass/thickness at pH 2.0 for all temperatures studied; raising the temperature from 20 up to 80°C leads to a 2–3 times increased mass at all values of pH (2.0–6.0) of the solutions. The enhancement of pH and the agitation speed of the media lead to higher tendency to anode passivity of the steel.

The physical methods applied in the investigation have identified the composition, probable compounds, structure and roughness of the amorphous phosphate coatings obtained.

References

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