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A simple testing method for quality control of phosphate coatings based on impedance measurements☆

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Abstract

A simple technique for quick quality control of phosphate layers based on impedance measurement has been developed. The coverage of iron surfaces by insulating phosphate crystals is the most important measure of the corrosion protection ability of the layers. From the detailed analysis of the measured impedance we were able to determine the surface coverage which was found to be in very good agreement with the results of SEM (scanning electron microscopy) and WDS (wavelength dispersive spectroscopy) investigations. The results provided by the impedance analysis are reliable but for industrial quality control simpler methods are needed. Our purpose was to provide a fast, objective procedure characterizing the corrosion protection ability that is easily applicable in industry. In the present paper we propose a method based on electrode impedance measurements of phosphated steel surfaces but, instead of measuring the impedance in a wide frequency range, we only use one appropriate frequency and the imaginary part of the impedance is recorded.

1. Introduction

Conventional phosphate layer tests are phosphate layer weight determination [1], the saltwater test [2] and the copper sulfate probe [3]. In the quality control of phosphate layers there is a need for a fast measurement based on the basic corrosion protection properties that is an objective test. The measurement of the weight of the phosphate layer gives exact results but they are very loosely connected to the corrosion properties. For example, a small-grained phosphate layer with low weight can be more compact (providing better protection) than a phosphate layer built from bigger crystals. The copper sulfate probe and the saltwater test are effective corrosion tests but are subject to human error. They require visual evaluation with results often depending on the person performing the test. Methods that can correctly and objectively characterize the corrosion are electrochemical techniques which determine quantities like current or impedance from which the rate of metal dissolution can be calculated.

The corrosion preventing compounds of zinc phosphate layers are the insulating hopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$) and phosphophillite crystals ($Zn_2Fe(PO_4)_2 \cdot 4H_2O$) which do not continuously cover the iron surface. Amorphous vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) and conducting magnetite (Fe_3O_4) are present at the voids between the crystals at these spots corrosion can take place. The iron or steel surface incompletely covered by zinc phosphate layers can be considered as a partially blocked electrode. The properties of such electrodes can be determined by impedance measurements.

In previous work [4–6] we made a detailed evaluation of the corrosion protection properties of phosphate layers using impedance measurements, SEM and WDS pictures. The impedance measurements were performed in neutral $NaClO_4$ solution in equilibrium with air. We found a simple equivalent circuit that matches both the measured impedance data and the measuring conditions (Figure 1). The anodic iron dissolution, the simultaneously ongoing cathodic oxygen reduction process and the double layer capacity are represented by the resistor R_a, the diffusion impedance W and the capacity C_{dl}, respectively. We determined the values of the elements of the equivalent circuit and calculated the portion of the active (uncovered) surface area, κ, and the coverage, Θ by the following equations:

$$\Theta = 1 - \frac{R_{a0}}{R_a}, \quad \Theta = 1 - \frac{C_{dl}}{C_{dl0}}$$

and

$$\Theta = 1 - \kappa$$

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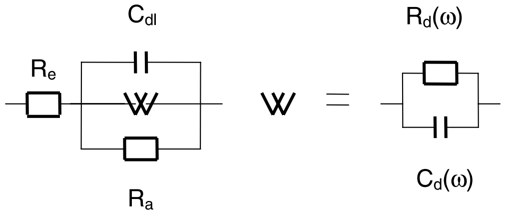


Fig. 1. Equivalent circuit representing the measured impedance.

where κ is the ratio of the active surface area to the total surface area. R_{a0} and C_{dl0} were determined from the impedance measured on samples which were treated by phosphoric acid (in the absence of any zinc compounds) having a concentration equal to that in the corresponding phosphating bath. The surface obtained in this way was assumed to be identical to that formed in the voids of the zinc phosphate crystals during phosphate treatment.

The case of the diffusion impedance is more complicated. Vetter [7] studied the diffusion processes on partially blocked electrodes and showed that the diffusion impedance (W) is inversely proportional to the quotient of the active surface area and the total surface area (κ). W can be considered as the parallel sum of two frequency dependent elements R_d and C_d (Figure 1):

$$R_d = \frac{1}{\kappa} \times \frac{RT}{n^2F^2Dc_0} \times \frac{1}{\sqrt{\frac{\omega}{2D}} + \frac{\sqrt{2}}{r_a}}$$

$$\frac{1}{\omega C_d} = \frac{1}{\kappa} \times \frac{RT}{n^2F^2Dc_0} \times \frac{1}{\sqrt{\frac{\omega}{2D}}}$$

where R, T and F are the universal gas constant, the absolute temperature and the faradaic constant, respectively, n the number of electrons exchanged in the electrode reaction, D the diffusion constant, ω the angular frequency, c_0 the bulk concentration of the species transported to the surface by diffusion, and r_a the average linear size of the active spots of the surface.

R_d and $1/\omega C_d$ plotted as a function of $1/\sqrt{\omega}$ gives straight lines (R_d vs $1/\sqrt{\omega}$ is linear if $\sqrt{2}/r_a$ is negligible compared to $\sqrt{\omega/2D}$). Then Θ and κ can be obtained from the slopes measured on samples treated with phosphoric acid only ($m_{R_{d0}}$, $m_{C_{d0}}$) and on the surface treated with the actual phosphating bath ($m_{R_{dph}}$, $m_{C_{dph}}$):

$$\Theta_{R_d} = 1 - \frac{m_{R_{d0}}}{m_{R_{dph}}} \quad \text{and} \quad \Theta_{C_d} = 1 - \frac{m_{C_{d0}}}{m_{C_{dph}}}$$

From the impedance diagrams we determined the equivalent circuit elements: R_a, C_{dl}, $R_d(\omega)$ and $C_d(\omega)$ and calculated the coverage values of the phosphate layers separately from each. The coverage was calculated for samples, which were treated for different periods of time, and we followed how the phosphate layer was built up. Other authors also found that the coverage is an important feature of the phosphate layer [8–10].

The detailed analysis described briefly above is appropriate for research and helps in the development of new treatments, but is time consuming and is too complicated in everyday quality control. Based on impedance measurements we worked out a simple test that can be used for quality control of phosphate layers in the laboratory and in industry.

2. Experimental details

Samples were prepared from three different commercially used phosphate baths. In the preparation step the cold rolled steel plates were degreased and then pickled. Both steps were followed by thorough rinsing. After phosphating the samples were rinsed and dried. The time of phosphating was varied during each set of experiments in order to follow the formation process of the phosphate layer. The samples were kept in dry air at room temperature until the impedance measurements were started.

The impedance was measured under potentiostatic conditions at open circuit potential with a three-electrode cell in a neutral 0.1 mol dm^{-3} sodium perchlorate electrolyte in equilibrium with air. The working electrode was the phosphated steel sample under investigation, the counter electrode a stainless steel disc in a parallel arrangement to the working electrode, while a calomel electrode equipped with a Luggin capillary was used as reference.

The impedance measurements were performed using a Solartron FRA 1250 frequency response analyser and a 1286 electrochemical interface. The amplitude of the perturbing voltage signal was 1 mV$_{\text{eff}}$, 4 points per frequency decade were measured in the frequency range of 56 kHz–0.1 Hz. The data were collected and evaluated using a PC.

In addition to the electrochemical impedance measurements conventional tests were also made: phosphate layer weight determination, the saltwater test and the copper sulfate probe. The weight of the phosphate layer was determined as a difference between the weight of the samples before and after chemical dissolution of the layer from the iron. The saltwater test and the copper sulfate probe both needed visual evaluation. In the first case the phosphated sample was immersed for 15 min in deionized water containing 3% NaCl and the samples were considered to be good if there was no corrosion damage visible on the surface. In the second case a solution containing $CuSO_4$, NaCl and HCl was dropped on the surface of the sample and the time of the appearance of the colour of the deposited copper was measured.

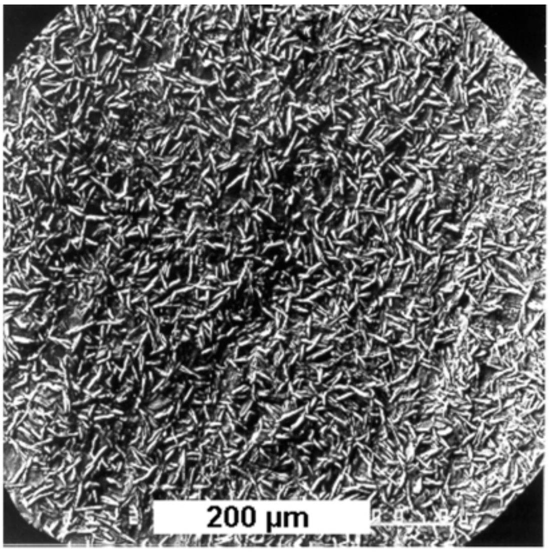
3. Results and discussion

The impedance evaluation procedure of our previous work [6] was followed and the coverage values were determined. Figure 2 shows the SEM pictures of the samples prepared from baths denoted A, B and C. The shapes and the sizes of the crystals forming the layers are very different and this affects the properties of the phosphate layers. Figure 3 shows the impedance diagrams for phosphate layers prepared from baths denoted A, B and C while in Figure 4 the coverage calculated from the impedance as a function of phosphating time is presented. The coverage against phosphating time curves clearly show that the coverage increases in time. After an optimal time the quality of the phosphate layer tends to deteriorate, especially in the case of layer B.

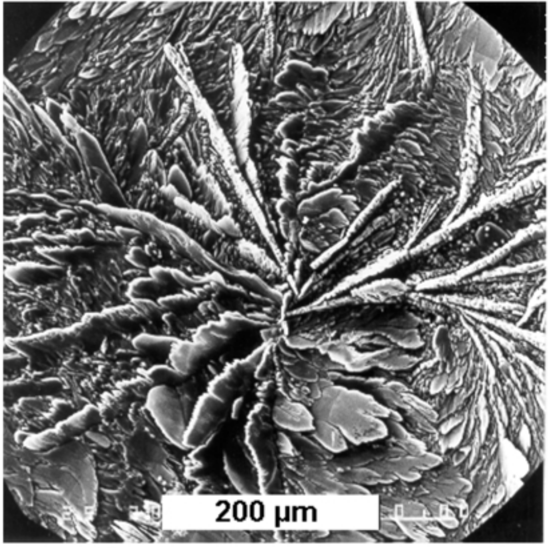
The coverage values calculated on the basis of the double layer capacity and diffusion impedance are in good agreement, while those obtained from polarization resistance are smaller than the previously mentioned ones, probably due to dissolution of the thin, amorphous layer in the voids of the zinc phosphate crystals influencing the kinetics of metal dissolution.

Taking a closer look at the impedance diagrams taken at various conditions the impedances corresponding to frequencies higher than 5 Hz are on the uprising part of the capacitive arc of the impedance diagram. As the arc of the impedance diagram is larger if the corrosion protecting property of the phosphate layer is better, the point corresponding to a certain frequency over about 5 Hz on the arc is shifted to higher impedance values. This means that the impedance measured at a selected frequency in this range can also be used to characterize the quality of the layer. Since the impedance can be measured more accurately if it is higher, the most appropriate frequency is 5 Hz, which is the lowest one that fulfils two criteria for all the three investigated systems: the impedance point belonging to this frequency must be on the uprising part of the arc on all diagrams and at the same time should correspond to a high impedance. (For systems A and C lower frequencies could also be appropriate according to the criteria, but not for layer B.) The impedance measured at 5 Hz can be used for a numerical characterization of the phosphate layer. The measurement can be even simpler if we measure only the imaginary part of the impedance. We chose the imaginary part of the impedance because in this way we do not have to determine and subtract the Ohmic resistance that is included in the real part of the impedance. If we ensure that the measured surface areas are the same we will have a single number representing the protection properties of the phosphate layer. The advantage of the simple single frequency impedance method is that it can be carried out with a small inexpensive instrument designed for that specific task.

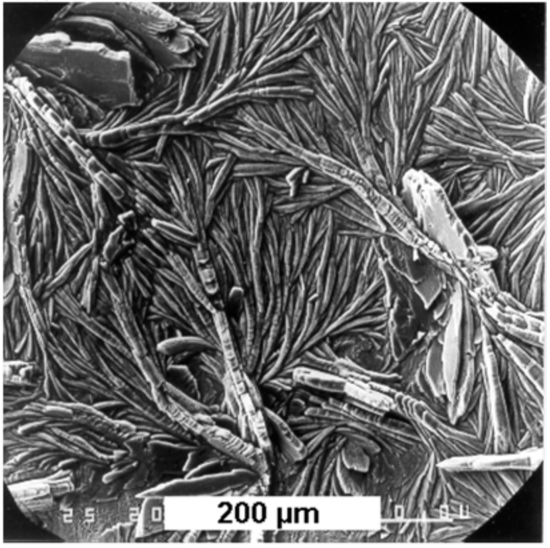
The measuring cell can be set up very quickly and easily: a simple glass tube is glued perpendicularly on the investigated surface and is filled up with 0.1 mol dm^{-3} sodium perchlorate solution. Generally after about 20 min (when the system is stabilized) the counter and reference electrode are immersed in the electrolyte and the impedance at 5 Hz is measured. This arrangement is suitable for rapid measurements on a series of samples. The time for impedance measurement moving the counter and reference electrode into the cell and setting



Layer A



Layer B



Layer C

Fig. 2. SEM pictures of phosphate layers made from three different baths.

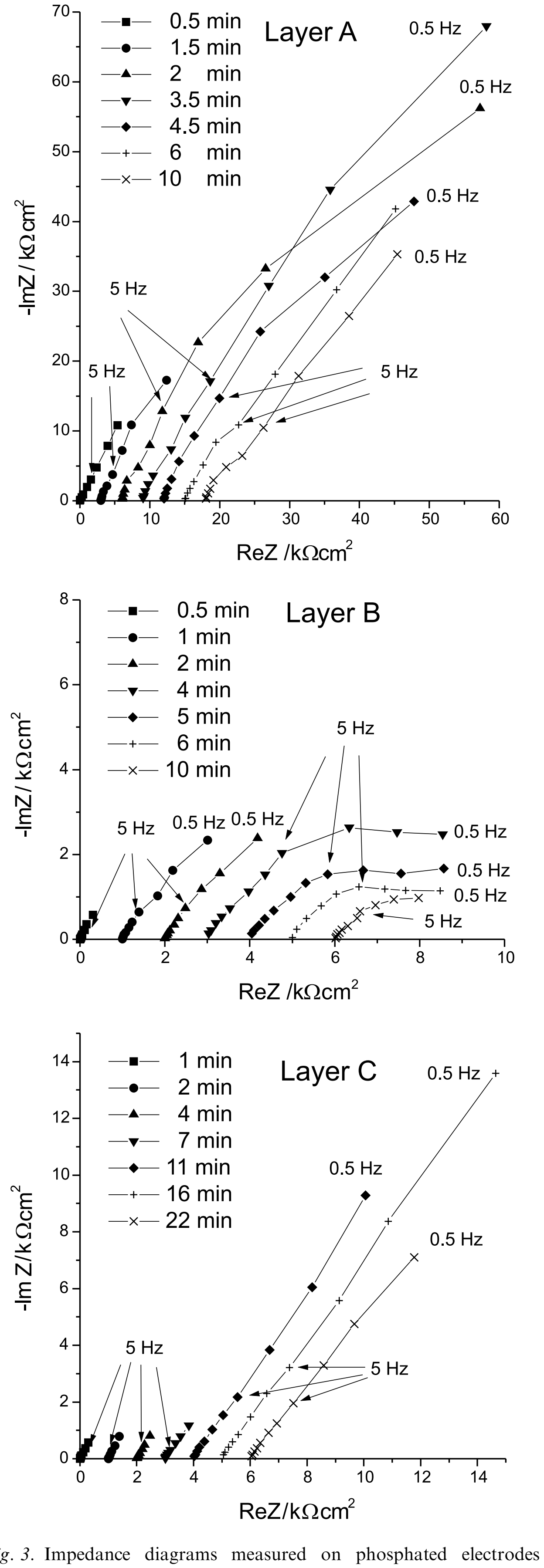


Fig. 3. Impedance diagrams measured on phosphated electrodes treated for different times for the three layers. Successive curves are shifted horizontally by 3, 1, and 1 kΩ, respectively.

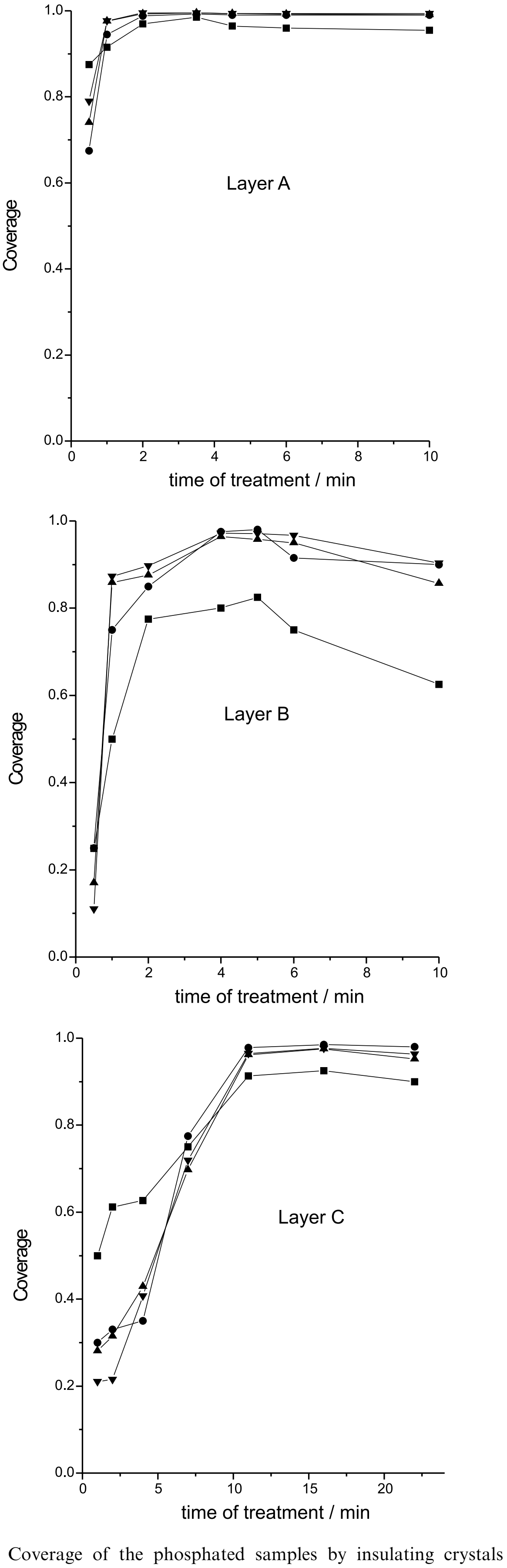


Fig. 4. Coverage of the phosphated samples by insulating crystals calculated from the elements of the equivalent circuit for the three layers. Key: (■) R_a, (●) C_{dl}, (▲) R_d (ω), (▼) C_d (ω).

Table 1. Comparison of the results of conventional and impedance measurements based testing methods on three different types of phosphate layers made on cold rolled steel samples

Layer	Time of phosphating/min	Coating weight/g m^{-2}	Copper sulfate probe/s	Saltwater test	Coverage	$-\mathrm{Im}\, Z(5\ \mathrm{Hz})/\mathrm{k}\Omega\ \mathrm{cm}^2$
A	0.5	1.2	8	bad	0.67	0.9
	1.5	3.7	15	good	0.94	3.9
	2	4.2	18	good	0.98	13.3
	3.5	4.4	20	good	0.99	17.8
	4.5	4.5	22	good	0.99	15.2
	6	4.6	21	good	0.99	11.3
	10	4.8	21	good	0.99	10.9
B	0.5	5.5	7	bad	0.25	0.1
	1.0	8.2	14	bad	0.75	0.7
	2	11.3	19	good	0.85	0.8
	4	12.9	29	good	0.97	2.2
	5	13.4	33	good	0.98	1.6
	6	14.6	35	good	0.92	1.3
	10	15.2	19	good	0.90	0.8
C	1	0.9	4	bad	0.30	0.12
	2	3.9	5	bad	0.33	0.15
	4	8.4	6	bad	0.35	0.2
	7	13.3	9	bad	0.78	0.3
	11	17.5	33	good	0.98	2.3
	16	18.6	37	good	0.99	3.4
	22	18.9	31	good	0.98	2.0

the open circuit potential takes about 2 min, while a sequence of measurements on 10 samples takes altogether about 40 min, including the set-up of the cells and the waiting time while the system stabilizes.

Table 1 lists the results of different conventional tests, the coverage calculated from the double layer capacity values, and the imaginary part of the impedance measured on an equal area of the samples as a function of phosphate treatment time. The coating weight shows a continuous increase with time and, after an optimal time corresponding to phosphate treatment, the layer weight continues to increase but at the same time the corrosion protection quality, the coverage and the copper sulphate probe results of the layer will decrease. This behaviour is obvious because the individual crystals are oriented at random and as they grow they touch, damage one another or push one another off the surface. As a result, the quality of the layer decreases when the crystals become too large. After the optimal treatment time the copper sulphate probe indicates only a slight decrease in quality, because through the thickened phosphate layer it becomes more and more difficult to recognize the colour of the deposited copper. The saltwater test is insufficiently sensitive to determine the optimal treatment duration because it can only determine whether the layer is good or bad. Table 1, on the other hand, shows that the impedance is a very sensitive measure of the phosphate layer quality. The build-up and the degradation process of the phosphate layer with time is shown magnified compared to the other tests. This makes this technique appropriate for the characterization of phosphate layers and for optimization of phosphate treatment technologies.

4. Conclusions

We have investigated impedance diagrams obtained on phosphated steel electrodes and shown that the imaginary part of the impedance at a certain frequency is a sensitive measure of the corrosion protection ability of the investigated phosphate layers if the frequency fulfils three criteria: (i) the frequency should be on the uprising part of the capacitive arc of the impedance diagram; (ii) it should be the lowest such frequency; (iii) if several phosphating treatments are to be tested the appropriate frequency should fulfil criteria (i) and (ii) for all systems. Under such conditions the imaginary part of the impedance measured at the selected frequency is roughly related to the corrosion rate obtained with full impedance spectroscopy, and can be applied for comparative purposes. The method is very useful in determining the optimal phosphate treatment technology: it can replace conventional methods that are subject to human error and often do not reflect the corrosion protection properties of the layer. The method also provides a numerical characterization of the quality of the phosphate layer; these data can be collected via automatic data acquisition. The method requires a very simple apparatus and can be performed very rapidly and efficiently when a series of samples is to be tested. The apparatus can also be used under industrial conditions.

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