



Behaviour of intact and scratched phosphate coatings on zinc, zinc–nickel and mild steel in dilute sodium phosphate solution

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Abstract

Impedance measurements were performed at room temperature in a 0.005 M Na₂HPO₄ solution on steel and on electrodeposited Zn and Zn–12%Ni before and after phosphating. It was found that potential and impedance parameters (R_{ct} and C_d) for phosphated materials attained nearly steady values within about 20 min, indicating that this solution did not cause meaningful changes in phosphate coatings and that it could therefore be used for the quality evaluation of these coatings. On scratches in phosphate coatings on Zn or Zn–12%Ni phosphate deposits rapidly formed, probably owing to enhanced dissolution of the locally exposed substrates at the nobler potentials of the coated materials. This demonstrates that damaged coatings can easily recover on Zn substrates in a non-aggressive phosphate solution. It is suggested that the formation of phosphate deposits on bare metal amidst phosphate coatings should be taken into account in the porosity determination by chemical or electrochemical methods.

1. Introduction

Phosphate coatings are widely used to improve paint adhesion, corrosion resistance, lubrication and to provide electrical insulation [1–5]. The typical phosphating process involves dissolution of a base metal in an acidic solution of soluble primary phosphates, with the subsequent hydrolysis of these phosphates and the precipitation of insoluble tertiary phosphates.

Protective properties of paint/phosphate coatings may deteriorate due to the penetration of water and aggressive chloride and sulphate anions from the environment, and possibly also due to dissolved phosphate anions which have been found to cause corrosion under paint [6]. Phosphate anions can be present in the coatings as a result of insufficient rinsing after the phosphating treatment, and they may form under natural conditions due to solubilization of the coating constituents in penetrating moisture.

Despite the possible corrosive effect of phosphate anions, a dilute sodium phosphate solution (0.005 M Na₂HPO₄) was shown to be appropriate for evaluation of phosphate coating quality [7]. Other solutions and methods used for determination of porosity of phosphate coatings have been quoted in the latter publication. For evaluation of porosity it is required that the test solution will not introduce noticeable degradation of the coating; fulfilment of this requirement will be manifested by a possibly rapid attainment of steady

electrochemical conditions, and by a strong differentiation in electrochemical behaviour of phosphated and non-phosphated materials. A significant differentiation in the above solution was indicated by the strongly different impedance parameters [7]; however, stability of these parameters was not determined.

In the present work, the behaviour of unphosphated and phosphated materials was examined in 0.005 M Na₂HPO₄ in connection with the prospective use of this solution for the quality evaluation of phosphate coatings. The aim of the work was to determine the effect of the duration of immersion in 0.005 M Na₂HPO₄ on impedance parameters in order to estimate the occurrence of changes induced by this solution in the coatings. Bare metal in pores was simulated by scratches made in the coating. Scratches can also represent local mechanical damage in paint/phosphate systems.

The study was made on unphosphated and phosphated low-carbon steel, both unplated and plated with Zn and Zn–12%Ni. Characterization of the zinc-based coating systems is described elsewhere [8, 9]. The automobile industry uses a variety of pre-coated steels which include Zn, Zn–Ni and Zn–Fe electroplated coatings; for Zn–Ni coatings, the highest corrosion resistance in salt spray test is exhibited for 12 wt % Ni, hence the coatings with this Ni content are usually used [10].

Electrochemical behaviour of the materials was studied using electrochemical impedance spectroscopy (EIS);

this technique was also used to investigate the phosphating processes in real time [11, 12].

2. Experimental method

Materials were commercial products of the Kawasaki Steel Corporation, Japan, manufactured for automotive body panels. The following materials were used: (a) Zn-electroplated cold-rolled steel (designated in this work as 'Zn'), the Zn coating weight was 20 g m^{-2} (thickness about $4 \mu\text{m}$); (b) Zn-12 wt % Ni electroplated cold-rolled steel (designated as 'Zn-12%Ni'), the coating weight was 20 g m^{-2} (thickness about $2.5 \mu\text{m}$); and (c) unplated cold-rolled steel (C 0.02, Mn 0.13, P 0.023, Cr 0.04, Al 0.04, and the other elements each $\leq 0.01 \text{ wt } \%$) (designated as 'steel'). Phosphating of these substrates was performed by the Palbond L3020 treatment of the Nihon Parkerizing Company; the treatment was carried out at 40°C for 120 s. The phosphate coating weight was 2.5 g m^{-2} (mean thickness about $2.5 \mu\text{m}$) for each of the substrates. Samples of 16 mm in diameter were punched from sheets.

Measurements were made at room temperature in non-deaerated $0.005 \text{ M Na}_2\text{HPO}_4$ solution, (pH 8.5). The solution was prepared from an analytical reagent grade chemical and deionized water.

Samples were mounted in a flat specimen holder (EG&G PAR) with an exposed surface area of 1.0 cm^2 . Potentials were measured and reported relative to a saturated calomel electrode (SCE).

Impedance measurements were carried out at open-circuit potentials, with a Solartron Schlumberger 1255 HF frequency response analyser in conjunction with an EG&G PAR potentiostat/galvanostat (model 273). A potential sine signal of peak-to-peak amplitude 10 mV was superimposed on the open-circuit potential. The frequency ranged from 20 kHz down to 0.01 Hz. The instruments were operated through the electrochemical impedance software ZPlot for WindowsTM, and results were analysed with graphing and analysis software ZView for WindowsTM.

The behaviour of bare substrate surrounded by a phosphate coating was examined on scratched phosphated materials. Scratches were made with a steel blade along the diameter of the samples; they were 10 mm long and about $10 \mu\text{m}$ wide on Zn substrate and about $80 \mu\text{m}$ wide on Zn-12%Ni and steel substrates. Scratched samples were examined by SEM and electron probe X-ray microanalyser (EPM) before and after exposure to the test solution.

3. Results

3.1. Impedance measurements

EIS measurements were made at open-circuit after exposure to the test solution for 20, 50, 80 and

110 min. Data in the complex plane are presented for unphosphated and phosphated materials in Figures 1 and 2, respectively. Regular semicircles were observed for unphosphated Zn, whereas data for other materials

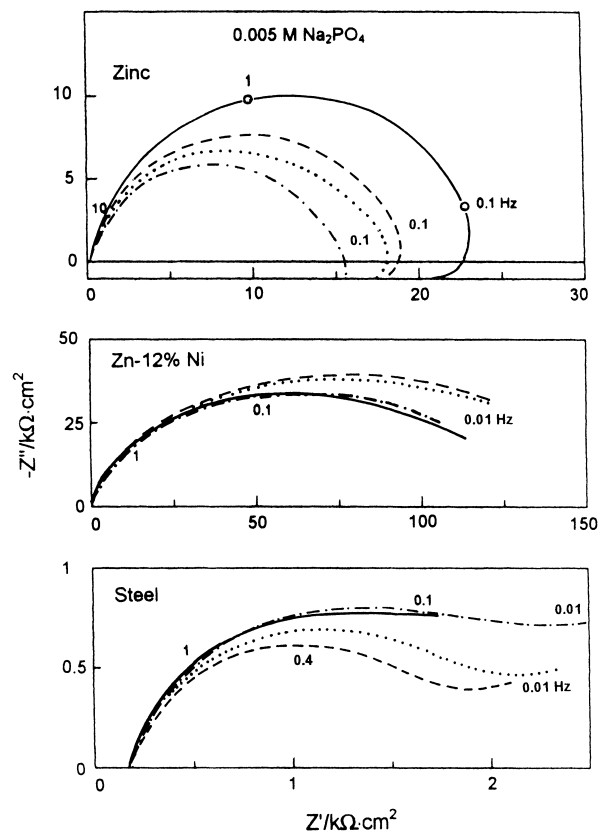


Fig. 1. Impedance results for unphosphated Zn, Zn-12Ni and steel in $0.005 \text{ M Na}_2\text{HPO}_4$ after immersion for (—) 20, (---) 50, (····) 80 and (- · - · -) 110 min.

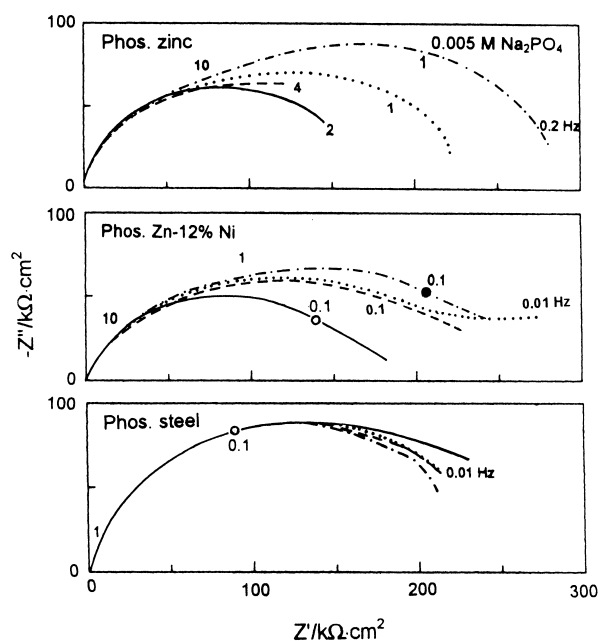


Fig. 2. Impedance results for phosphated Zn, Zn-12Ni and steel after immersion for the times as given in Figure 1.

showed parts of semicircles only in the high frequency region, with a considerable distortion at low frequencies. Such distortion is usually associated with mass transfer impedance [13–15]. In the case of semiinfinite linear diffusion, the linear behaviour is observed on the complex plane plots at low frequencies, whereas in the case of spherical diffusion, depressed semicircles are formed [15]. Turgoose and Cottis [16] derived the expected electrochemical impedance response of a corroding metal under conditions where diffusion is restricted by surface films. It was shown that with only slightly restricted diffusion, the reversible anodic reaction gives rise to two time constants, the first being related to the kinetics of the reversible reaction, and the second arising from a finite length diffusion impedance. The distortion of semicircles at low frequencies occurs for corroding systems with diffusion [17]. Based on these analyses of impedance response, the observed low-frequency distortion in Figures 1 and 2 can be ascribed to transport limitations.

The results indicate impedance changes with extension of exposure time as follows:

(a) *For unphosphated materials (Figure 1)*

Zn: diameters of the semicircles decreased, demonstrating a drop in the charge transfer resistance, without a contribution of diffusion; a loop in the low frequency region may indicate an inductive effect [17];

Zn–12%Ni: impedance tended to increase in the low frequency region, suggesting a rise of the diffusion contribution;

Steel: impedance initially decreased and then increased, mainly in the low-frequency region.

(b) *For phosphated materials (Figure 2)*

For all the materials the high frequency parts of the semicircles changed little, demonstrating an almost steady charge transfer resistance; at low frequencies the impedance increased very strongly for Zn and less strongly for Zn–12%Ni, manifesting the increasing contribution of diffusion, particularly for Zn. For phosphated steel the impedance changed slightly with time and, in contrast to Zn and Zn–12%Ni, it decreased in the low-frequency part.

These results indicate that during immersion in 0.005 M Na₂HPO₄, unphosphated zinc underwent activation, whereas unphosphated Zn–12%Ni and steel acquired surface layers which increased the diffusion limitations (Figure 1). The spectra for phosphated materials (Figure 2) suggest that on the phosphated Zn a surface layer developed which caused a strong diffusion impedance; on the phosphated Zn–12%Ni a surface layer led to a smaller diffusion limitation, whereas on the phosphated steel the formation of the diffusion-controlling layer was hindered.

The high frequency parts of the semicircles represented a simple electrochemical system which can be

represented by an equivalent circuit $R_o(C_d R_{ct})$ [15, 18–20], where R_o is resistance of the solution, C_d is a double layer capacitance, and R_{ct} is charge transfer resistance. Impedance data for the high-frequency part were analysed graphically using ZView Software. R_{ct} was estimated from the extrapolated diameter of the semicircles, and C_d was estimated from the relationship $C_d = (\omega|Z|)^{-1}$ for a straight line on a log|Z| Bode diagram. The slope of the line was often smaller than –1, so in these cases the values obtained cannot be ascribed to pure capacitance, because they also involve other processes, mainly slow diffusion [13–17] and/or slow adsorption [21].

Values of R_{ct} and of open-circuit potential for unphosphated and phosphated materials as a function of immersion time are shown in Figure 3, and values of C_d are shown in Figure 4. These figures indicate the following:

- Only R_{ct} for unphosphated Zn decreased regularly with the immersion time, whereas for other materials R_{ct} and C_d changed very slightly, demonstrating that reactivity of the latter materials remained fairly stable. This indicates that steady electrochemical conditions, which are required for porosity testing, are rapidly attained in the solution used.
- R_{ct} and open-circuit potentials were higher for phosphated materials than those for unphosphated substrates, whereas C_d were lower. This shows a significant difference in electrochemical behaviour of phosphated and unphosphated materials, and justifies the use of 0.005 M Na₂HPO₄ for the quality evaluation of phosphate coatings.
- For phosphated materials, values of R_{ct} were similar to each other, whereas values of C_d differed strongly. Different C_d might be associated with different porosity, however, in the earlier work [7] it was shown that values of C_d and R_{ct} for a 20 min immersion gave a realistic evaluation of the phosphate coating porosity only for Zn and steel (evaluated porosity was 1 to 9%), but not for Zn–12%Ni (evaluated porosity was 23 to 36%). It was suggested that electrochemical reactions occurred over an area larger than the surface exposed in the pores. In addition to this, during immersion the metal/coating interfaces may undergo changes, and the degree of these changes might vary for different materials.

Changes of the metal/coating interfaces due to immersion in 0.005 M Na₂HPO₄ were studied with SEM and EPM on scratched phosphated materials.

3.2. SEM and EPM on scratched phosphated materials

Figure 5 shows micrographs of phosphated materials with scratches, before immersion and after 1 h immersion. Remarkably, on scratches on the Zn substrate a deposit with needle-like crystals formed, suggesting a Zn-containing phosphate. On Zn–12Ni a deposit formed occasionally, whereas on steel it did not form at all. Other micrographs of scratches on phosphated Zn

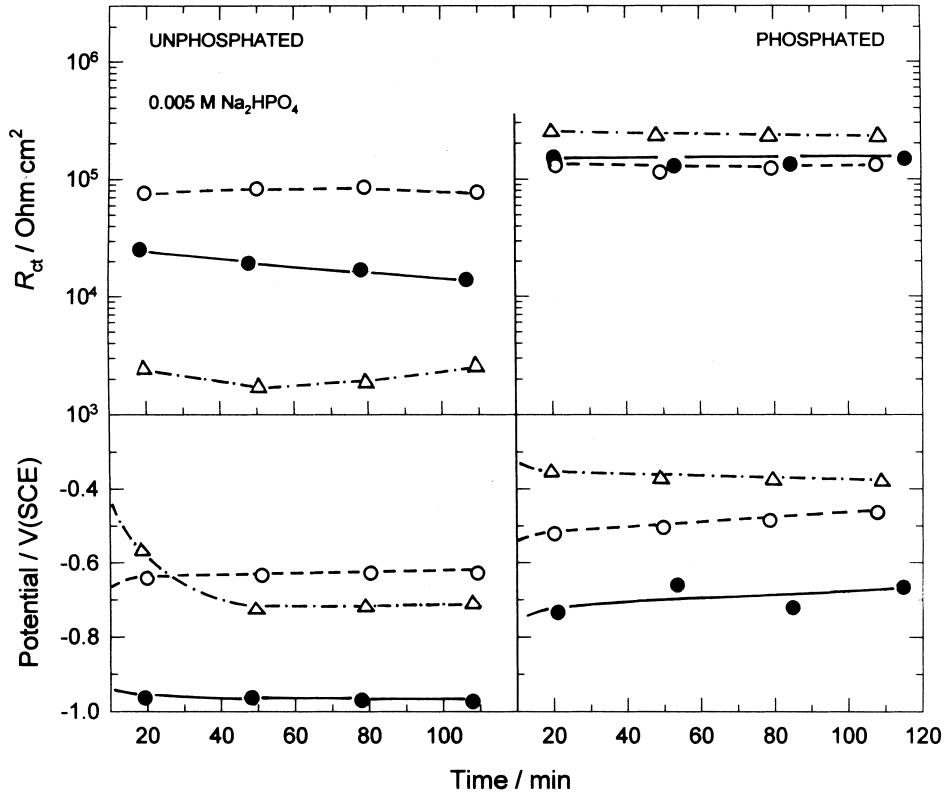


Fig. 3. Charge transfer resistance (R_{ct}) and open-circuit potential for unphosphated and phosphated Zn (●), Zn-12%Ni (○) and steel (Δ) as a function of exposure time in 0.005 M Na_2HPO_4 .

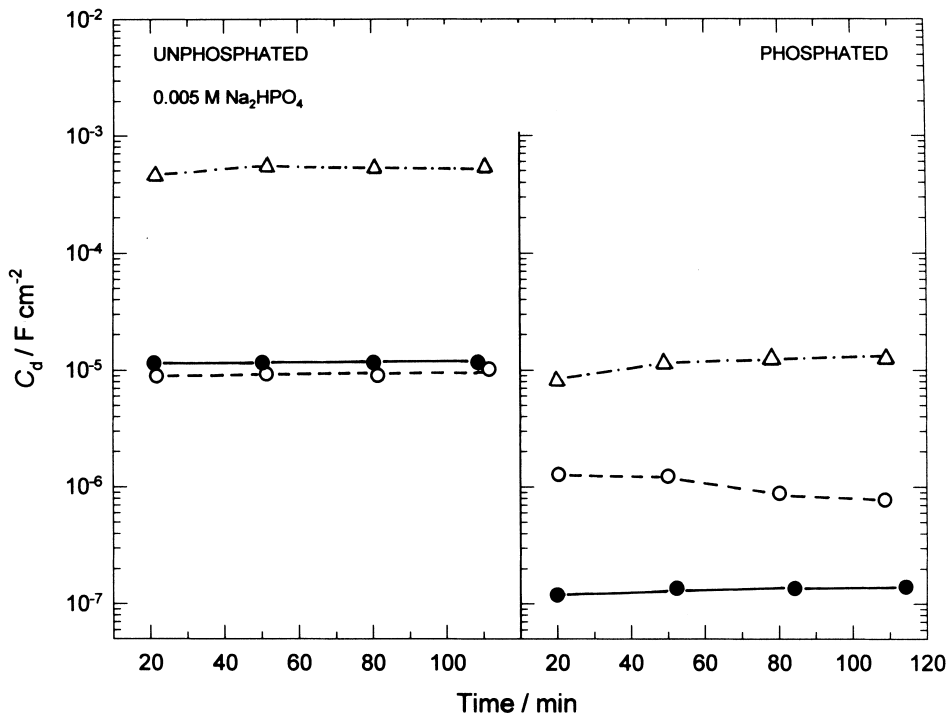


Fig. 4. Double layer capacitance (C_d) for unphosphated and phosphated Zn (●), Zn-12%Ni (○) and steel (Δ) as a function of exposure time in 0.005 M Na_2HPO_4 .

and Zn-12Ni after immersion (Figure 6) show that the new deposit on Zn was fine crystalline in the vicinity of the phosphate coating, and more coarse crystalline in the centre. On Zn-12Ni after a 15 min immersion the

deposit was formed on only a part of the scratch, while another part remained intact.

SEM and EPM images of scratched phosphated Zn before and after a 1 h immersion are shown in Figure 7.

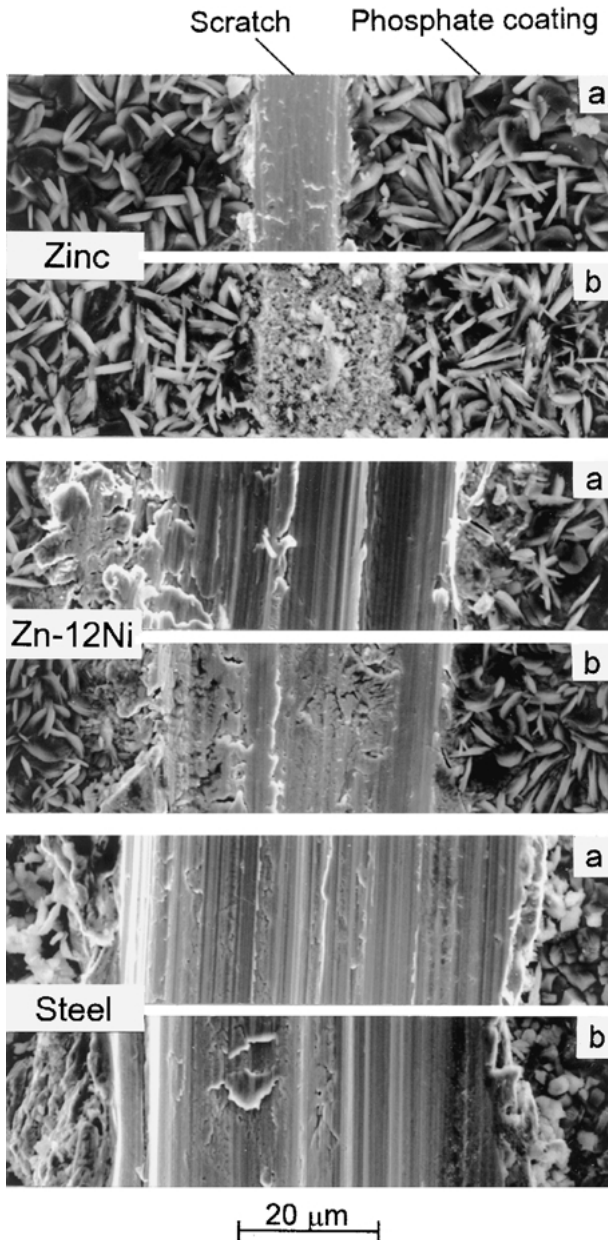


Fig. 5. SEM micrographs of phosphated materials with scratches, before immersion (a) and after a 1 h immersion in 0.005 M Na_2HPO_4 (b).

SEM shows the formation of a deposit on the scratch after immersion. EPM images before the immersion show the appearance of Fe areas on the scratch, indicating that the steel substrate was partly uncovered; accordingly, the intensity of the Zn signal was lower on these areas. The scratch was free of P, but contained some O. After 1 h immersion the intensity of P and O on the scratch was roughly the same as that on the intact coating, demonstrating the formation of a phosphate deposit on this scratch. On Fe-rich areas there appeared less Zn and slightly less P and O than elsewhere, indicating a smaller amount of a phosphate deposit on these areas. This shows that a phosphate deposit was very easily formed on the Zn substrate, whereas its formation on Fe was hindered.

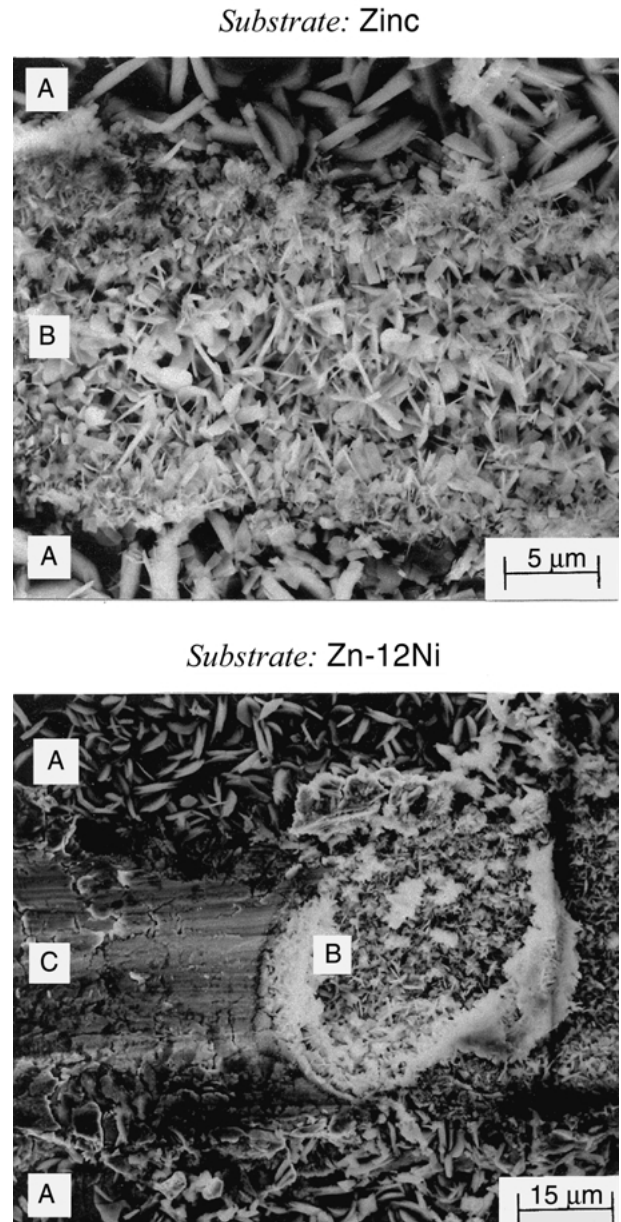


Fig. 6. SEM micrographs with scratches after immersion of phosphated Zn for 1 h and of phosphated Zn-12Ni for 15 min; (A) phosphate coating, (B) deposit on a scratch, (C) unchanged scratch.

4. Discussion

Variations in impedance of phosphated materials during exposure in 0.005 M Na_2HPO_4 are associated mainly with processes on the bare substrate in the pores, and these processes are similar to those on the scratches. From the behaviour of the scratches (Figures 5–7) it can be deduced that a new phosphate deposit can readily form in the pores on the Zn substrate, and less readily on the Zn-12%Ni substrate, but it cannot form on the steel substrate. The formation of the new deposit may lead to increased diffusion limitations, as indicated by the enlarged impedance in the low frequency parts (Figure 2). The diffusion impedance changed with time in agreement with the observed behaviour of the materials: a slight decrease in this impedance for steel

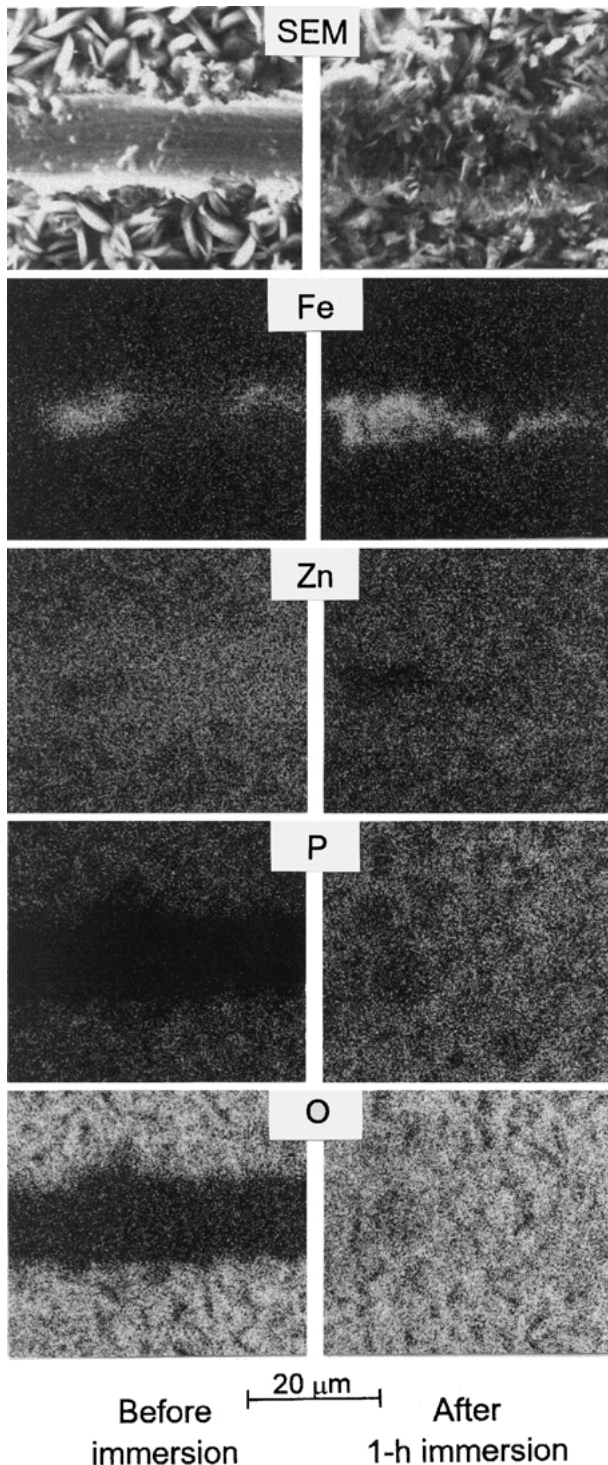
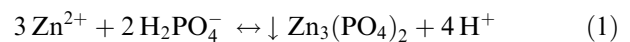


Fig. 7. SEM and electron microprobe X-ray images on a scratched phosphate coating on Zn coated steel, before and after a 1 h immersion in 0.005 M Na₂HPO₄.

is probably due to passivation, whereas the increase in the impedance for the Zn containing substrates is likely due to the growth of the new deposits. The higher increase for the Zn substrate corresponds to more intense formation of these deposits. The double layer capacitance C_{dl} for phosphated materials (Figure 4) appears to be inversely related to the intensity of the deposit growth, but the reason is not clear.

The dilute sodium phosphate solution used in this study did not induce deposition of phosphate coatings on the metallic substrates themselves. The lack of phosphating was indicated by values of charge transfer resistance and potentials both being lower than those for phosphated materials (Figure 3). This was confirmed by microscopic observation. However, this solution caused deposition of phosphates on Zn and on Zn–12Ni, if these substrates were locally uncovered amidst the phosphate coatings by scratching. Deposition was not observed on locally uncovered Fe substrates.

In a phosphating process, a base metal must dissolve fairly rapidly in a solution of soluble primary phosphates to produce a high concentration of metallic cations which subsequently leads to the precipitation of relatively insoluble tertiary phosphates [5]:



These processes are usually conducted in hot acidic solutions containing ions of the metal to be coated and oxidizing accelerators. Phosphate coatings can also be formed in primary alkali metal phosphates (e.g., NaH₂PO₄) without ‘coating’ metal ions, with the optimum pH of 4.0–6.0 [4].

In the present study the 0.005 M Na₂HPO₄ solution did not cause phosphating of the all-metal surfaces (apparently owing to its low concentration and higher pH). However, it was effective in the phosphating of Zn-containing substrates (particularly of Zn) amidst the phosphate coating. The latter effect can be explained by a shift of the open-circuit potentials in the noble direction, and by saturation of the solution with phosphates close to the phosphate coating. Figure 3 shows that the potentials of phosphated Zn are about 0.30 V nobler than those of the unphosphated substrate. It can be envisaged that bare substrate on the scratches will be polarised by the phosphate coating, and will undergo active dissolution due to the more positive potential. Faster dissolution will result in a higher concentration of dissolved Zn²⁺ cations and in an easier precipitation of tertiary phosphate (1). Precipitation can also be facilitated by the easier attainment of the saturation owing to partial dissolution of the existing phosphate coating. The appearance of the newly-precipitated deposit (Figure 6) provides some support for this explanation. Namely, the smaller size of the crystals adjacent to the existing coating can be explained by easier precipitation of the phosphate owing to the more positive potential (faster dissolution) and to the contribution of the phosphate dissolved from the coating.

Unlike Zn and Zn–12Ni, steel did not undergo phosphating on scratches, despite the very positive potential of the phosphated material (Figure 3). It is suggested that the lack of reactivity of scratches on steel is associated with the inhibiting action of phosphate anions on the dissolution of steel. Phosphates are widely used as corrosion inhibitors; they are effective especially in the presence of oxygen [22, 23], and they affect

corrosion of iron depending on their concentration and pH [24]. In a borate solution of pH 8.5, corrosion and film growth on Fe were retarded by the addition of small amounts of Na_2HPO_4 (0.01 M), but accelerated by the higher additions [25]. The low concentration of the solution used in this work favours the passivation of steel and prevents precipitation of phosphates owing to insufficient dissolution of iron.

The formation of a phosphate deposit on a scratched Zn substrate indicates that recovery of a damaged phosphate coating can occur easily on this substrate. Probably, the strong increase in impedance at low frequencies for phosphated Zn (Figure 2) is associated with phosphate formation in the pores. Under natural conditions in air, a phosphate solution is present in the pores of the coating due to its solubilization in penetrating moisture, and therefore healing of defects may occur spontaneously on this substrate. This suggests that, in practice, phosphate coatings might become free from real pores due to the occurrence of this healing process.

This implies a possible uncertainty in the evaluation of porosity by chemical or electrochemical methods. If a test solution induces the formation of a phosphate deposit on a bare metal at the bottom of pores, then the pores might not be detected. If a solution is aggressive and dissolves the coating, then the prior pores will be enlarged and new ones formed. A rapid attainment of nearly steady values of charge transfer resistance and of potential (Figure 3) indicates that 0.005 M Na_2HPO_4 belongs to the former category of test solution, and as pointed out in [7], it cannot exactly evaluate the real porosity. Owing to this uncertainty, there is a need for a more appropriate method for porosity determination.

5. Conclusions

- (i) Phosphated and unphosphated Zn, Zn–12Ni and steel attain nearly steady values of potential and impedance parameters (R_{ct} and C_d) within about 20 min in the 0.005 M Na_2HPO_4 solution. This indicates that this solution does not cause meaningful changes in phosphate coatings and is a good candidate for coating quality evaluation.
- (ii) In this solution, no precipitation of phosphates occurs on uniform metallic substrates. However, phosphate deposits form rapidly on small surface areas of Zn or Zn–12Ni substrates exposed by scratching of the phosphate coatings. The promoting effect of the coatings on phosphate precipitation can be explained by the shift in potential in the noble direction and by higher phosphate concentration in the solution adjacent to the coatings.
- (iii) The deposition of phosphates indicates that damaged coatings can easily recover on Zn substrates in non-aggressive solutions. Under real conditions, such solutions may be present in pores owing to solubilization of the coating constituents in penetrating moisture.
- (iv) In a similar manner to scratches, bare metal in coating pores may also undergo the recovery process. This implies that, in the case of Zn substrates in a dilute phosphate solution, real pores may disappear during immersion in the test solution.

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References

1. W. Machu, 'Die Phosphatierung' (Verlag Chemie, Berlin, 1950).
2. I.I. Khain, 'Theory and Practice of Phosphating of Metals' (in Russian) (Khimia, Leningrad, 1973).
3. G. Lorin, 'Phosphating of Metals' (Finishing Publications, Teddington, UK, 1974).
4. D.B. Freeman, 'Phosphating and Metal Pre-treatment' (Woodhead-Faulkner, Cambridge, 1986).
5. W. Rausch, 'The Phosphating of Metals' (ASM International, Metals Park and Finishing Publications, Teddington, 1990).
6. U. Stieglitz, W-D. Schulz and W-D. Kaiser, *J. Oberflächen technik* (1995) 44.
7. J. Flis, Y. Tobiya, K. Mochizuki and C. Shiga, *Corros. Sci.* **39** (1997) 1757.
8. G. Krauss and D.K. Matlock (Eds), 'Zinc-based Steel Coating Systems: Metallurgy and Performance' (TMS, Warrendale, 1990).
9. 'Proceedings of International Conference on Zinc and Zinc Alloy Coated Steel Sheet' (Iron and Steel Institute of Japan, Tokyo, 1989).
10. T. Irie, in G. Krauss and D.K. Matlock (Eds), 'Zinc-based Steel Coating Systems: Metallurgy and Performance' (TMS, Warrendale, 1990), p. 143.
11. N. Bretherton, G.E. Thompson and S. Turgoose, *Corros. Sci.* **35** (1993) 1297.
12. D.L. He, F.C. Chen, A.H. Zhou, L.H. Nie, S.Z. Yao, *Thin Solid Films* **382** (2001) 263.
13. J.E.B. Randles, in E. Yeager (Ed), 'Transactions of the Symposium on Electrode Processes' (Wiley, New York, 1959), p. 209.
14. S.R. Taylor and E. Gileadi, *Corrosion* **51** (1995) 664.
15. A. Lasia, in B.E. Conway, J.O'M. Bockris and R.E. White (Eds), 'Modern Aspects of Electrochemistry', No. 32 (Kluwer Academic, New York, 1999), p. 143.
16. S. Turgoose and R.A. Cottis, in J.R. Scully, D.C. Silverman and M.W. Kendig (Eds), 'Electrochemical Impedance: Analysis and Interpretation' (ASTM STP 1188, Philadelphia, 1993), p. 173.
17. B.A. Boukamp, in M.W. Kendig (Ed.), 'Computer Aided Acquisition of Corrosion Data' (The Electrochemical Society, Pennington, NJ, 1985), p. 146.
18. M. Sluyters-Rehbach and J.H. Sluyters, in A.J. Bard (Ed.), 'Comprehensive Treatise of Electrochemistry', Vol. 9 (Plenum, New York, 1984), p. 177.
19. J.R. Macdonald, 'Impedance Spectroscopy Emphasizing Solid Materials and Systems' (Wiley, New York, 1987).
20. C. Gabrielli, 'Use and Applications of Electrochemical Impedance Techniques'. Technical Report No 24 (Solartron, Instruments, Farnborough, UK, 1990).
21. T. Pajkossy, T. Wandlowski and D.M. Kolb, *J. Electroanal. Chem.* **414** (1996) 209.
22. M.J. Pryor and M. Cohen, *J. Electrochem. Soc.* **100** (1953) 203.
23. M.D. Kanonova, G.M. Floryanovitch and Ya.M. Kolotyrlin, *Zashch. Met.* **4** (1968) 315.
24. Z. Szklarska-Smialowska and R.W. Staehle, *J. Electrochem. Soc.* **121** (1974) 1393.
25. W. Kozłowski and J. Flis, *Corros. Sci.* **32** (1991) 861.