

Study on the chemical deposition on steel of zinc phosphate with other metallic cations and hexamethylenetetramine. II. Evaluation of corrosion resistance

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We studied the effect of the insertion with Co(II), Mg(II) and Ni(II) and of an surface agent (hexamethylenetetramine) of the zinc phosphate layer on steel plates. The samples were analyzed using SEM-EDX and the corrosion behaviour of phosphated coatings was determined by potentiostatic polarization. From the obtained data we were able to optimize solutions in order to obtain better corrosion resistance results for the phosphate layers.

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1. Introduction

Today, the industry requires many anticorrosion procedures for the protection of iron surfaces. In this purpose, thin, continuous and uniform layers are deposited on steel objects [1-6].

Regarding surface treatments on iron substrates, Zn phosphating is one of the most widely used. Acid aqueous phosphate solutions containing zinc ions and phosphoric acid are used. The phosphate coating develops via the nucleation, growth, and coalescence of zinc phosphate grains [4-10].

The known anticorrosion procedures of iron object surfaces by chemical phosphatation consist in precipitation in thin, continuous and uniform layer of low soluble pyrophosphate, as Zn(II), Ni(II), Mn(II), Ca(II) and, very rarely, Fe(II). More often is used zinc, singular or in mixture with the presented metals, in order to confer polychrome aspect. This procedures have the disadvantage that they involve a large number of cations in the composition of the in-situ obtained layers or of the paint layer, and also a high labor and time [11-17].

In the anodic area Fe^{2+} ions are formed (from the support) and contribute to the formation the primary layer of zinc pyrophosphate, the resulted crystalline structures becoming inert to oxidative processes [18-22].

There are known solutions with additives, such as Ni^{2+} , Mn^{2+} , Ca^{2+} and Mg^{2+} , in order to form a homogeneous phosphate coating with finer Zn phosphate grains. The presence of Ni^{2+} and Mn^{2+} in the phosphate solution apparently affects the nucleation and growth of the Zn phosphate grains [4-8, 23-25].

The paper presents the evaluation of corrosion resistance of new zinc phosphate layers on iron surfaces,

which have in composition next to the zinc phosphate also transitional metals phosphates as Co, Ni and Mg.

2. Experimental part

2.1. Materials and procedures

As support material round plates of mild steel DC 01 type, according to US standards: Carbon Steel AISI 1010 (SR EN 10130) were used, we selected 5 samples with different phosphate layers. The standard steel sample was named X0 and the other X1 to X5.

Before the layer deposition the steel plates were degreased for 10 minutes in mild alkaline bath and then pickled for half an hour in an acid solution. We started from an initial phosphate solution, containing 8.16 mL H_3PO_4 98%, Zn 4g, 2.6 mL HNO_3 60%, 0.75g NaOH, 0.45g NaNO_2 , 0.05g $\text{Na}_3\text{P}_3\text{O}_{10}$ for one liter of solution. In this solution samples named X1 were obtained.

By adding to the initial solution 12g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ per liter we obtained the samples named X2, by adding 12g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ per liter the sample X3 was obtained, and by adding 15g $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ the sample X4. Samples X5 were merged in initial solution with 2 g hexamethylenetetramine.

All the samples were merged for 30 mins in the phosphate solutions at 90 °C.

2.2. Analysis methods and techniques

A Tescan SEM VEGA II LSH was used for imaging and the corrosion tests were performed using an electrochemical cell with 3 electrodes connected to an

Autolab PG STAT 302 (Metrohm Autolab) Potentiostat. The software used in analyses is Nova 1.6. The reference electrode is a saturated calomel (ECS), the auxiliary electrode is made of platinum and the third one was the tested sample.

3. Results and discussions

In Fig. 1 are presented the SEM images of the samples with secondary electrons for X0 and back scattered electrons for X1-X5.

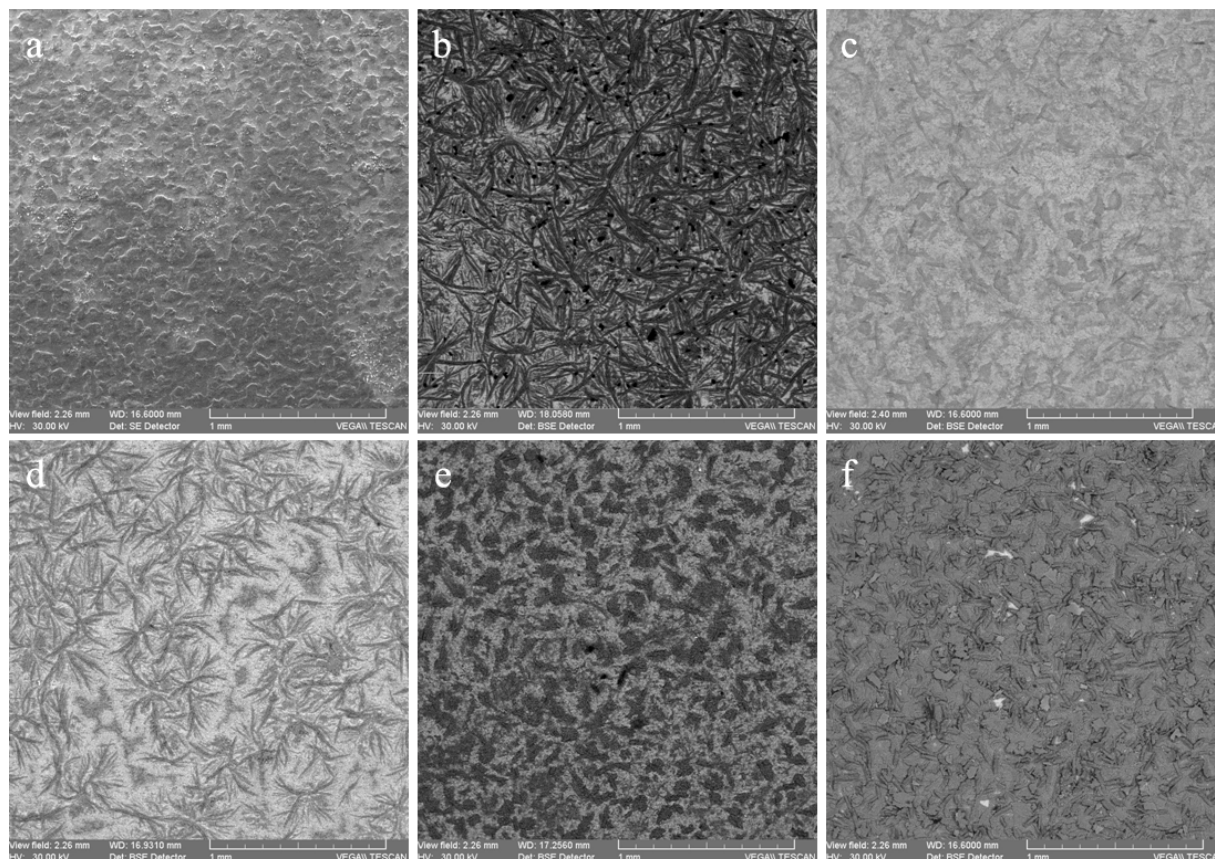


Fig. 1. The SEM images of the samples (100X): a – X0, b – X1, c – X2, d – X3, e – X4, f – X5

From the Fig. 1 we can observe the surface structure of the samples. The morphology of dendrites and the uniformity of the layers can be well defined. X1 sample presents thin and elongated dendrites, compared with X2 and X4 samples which are irregular with rare dendrites. In contrast, the samples X3 and X5 have an uniform and compact layer, with well-developed 3D dendrites, which makes the layer to be thicker.

The cyclic voltammograms (CV) of the six samples were recorded (standard sample and the ones with zinc phosphate layers) in the $-1.2 \div 1.8\text{V}$ range with a scanning speed of 100 mV s^{-1} . From here the corrosion in points and at the retour scan an histeresis curve has appeared, characteristic to this type of corrosion was determined [26, 27].

For the etalon sample (steel plate not covered) in a 0.1M NaCl solution, the passive range (fig. 2) is very narrow ($-0.55 \div -0.05\text{V}$) and the sharp increase of the anodic current reaches high values ($\approx 8\text{mA}$), after that the curve becomes flat. On the retour scanning of the potential, the current drops to low values, compared to the

sharp increase from the tour scanning. The histereris is very narrow.

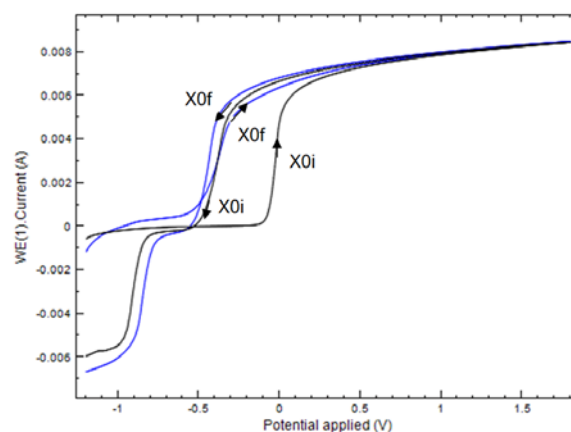


Fig. 2. CV for the standard sample in 0.1M NaCl solution ($X0_i$, tour and retour scan) and after 5 hours ($X0_f$).

The cyclic voltammogram for the X5 sample on $-1.2 \div 0.8\text{V}$ range shows that the sample is resistant on the interval. At 0.8V a sharp increase of the current appears until 6mA , probably because of the phosphate layer. In time the passive range is decreasing, because of the maintaining in solution. Thus, the corrosion resistance is decreasing.

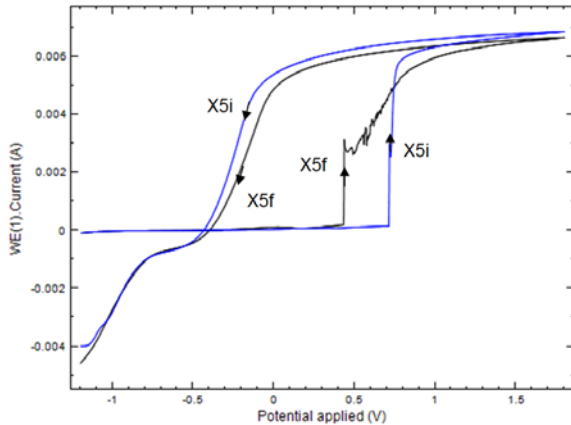


Fig. 3. CV for X5 sample in 0.1M NaCl solution ($X5_i$ tour and retour scan) and after 12 hours ($X5_f$)

For the samples X5 and X3 the CV are presented in figure 4, where the passive range doesn't exist for X3. In figure 5 is presented the CV for the X2 sample, which doesn't present a passive range, but also the tour scan doesn't evidentiate corrosion in points. As for the X4 sample, this has a very narrow passive range.

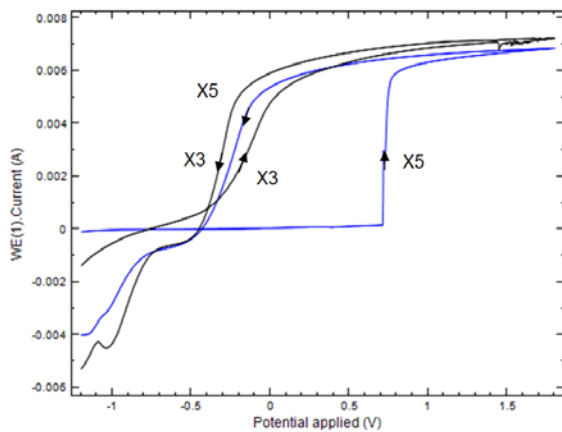


Fig. 4. CV for X5 and X3 samples in a 0.1M NaCl solution.

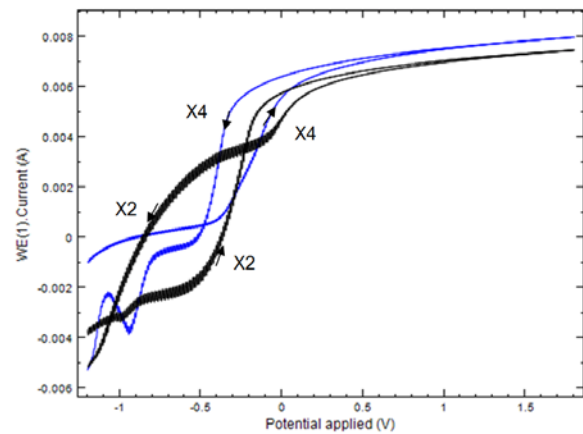


Fig. 5. CV for X2 and X4 samples in a 0.1M NaCl solution.

A very interesting behaviour has X1 sample (with zinc phosphate layer), which is resistant between -0.834 and -0.300V , after that a sharp increase of the current appears, in comparison with S1d sample (previously degreased and pickled), which doesn't present the passive range, only a flattening of the current on the interval $-0.558 \div -0.363\text{V}$, as shown in Fig. 6.

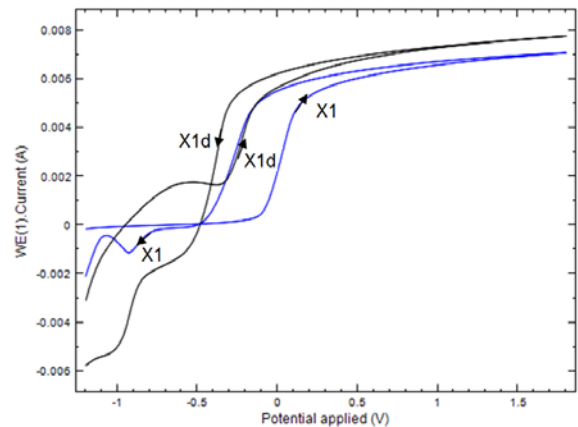


Fig. 6. CV for X1 sample in a 0.1M NaCl solution ($X1d$ – sample S1 which was degreased and pickled before the test).

Compared with X1, the X4 sample is more stable and more resistant, even though the passive range of X1 is higher (Fig. 7).

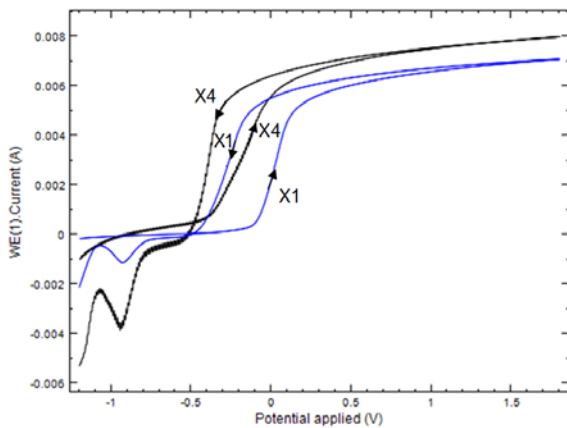


Fig. 7. CV for S1 and S4 samples in the 0.1M NaCl solution

For obtaining the corrosion speed the linear voltammograms were evaluated on the range of $\pm 150\text{mV}$ to the open circuit potential (OCP) of every sample, determined before were registered the linear voltammogram plotting. Using Nova 1.6 software the corrosion potential was calculated.

In order to calculate the corrosion speed, it was considered the oxidation of iron to $\text{Fe}(\text{OH})_2$ as is known in the literature [28,29], considering the current density, j , defined by Butler-Volmer relation [30]:

$$j = j_{cor} \left[\exp\left(\frac{2,303(E - E_{cor})}{b_a}\right) - \exp\left(-\frac{2,303(E - E_{cor})}{b_c}\right) \right] \quad (1)$$

where b_a and b_c are the Tafel slopes:

$$b_a = \frac{RT}{\alpha nF} \quad \text{respectively} \quad b_c = \frac{RT}{(1 - \alpha)nF} \quad (2)$$

The corrosion speed can be correlated with the intensity of the corrosion current or with the current density based on the general law of electrolysis.

The superficial corrosion speed is defined as the weight loss on time unit on surface unit, according to the relation:

$$v_s = \frac{\Delta m}{t \cdot S} \quad \text{or} \quad v_s = \frac{A}{zF} j_{cor} \quad (\text{g/cm}^2 \cdot \text{s}) \quad (3)$$

E – applied potential, Δm - weight loss during t time, I_{cor} – corrosion current, $K=A/zF$ is electrochimic equivalent of the corroded methal (A – atomic weight, z – number of the electrons involved in oxidation, $F = 96485 \text{ C/mol}$ – Faraday constant).

The corrosion speed was determined, being presented in Table 2.

Table 2. Corrosion speed of the samples in 0.1M NaCl solution.

Sample	-OCP (mV)	v_{cor} (mm year^{-1})
X3	450	$0.6554 \cdot 10^{-3}$
X5	395	$1.6078 \cdot 10^{-3}$
X4	414	$7.6022 \cdot 10^{-3}$
X2	506	$11.01 \cdot 10^{-3}$
X1	348	$33.882 \cdot 10^{-3}$
X0	513	$108.50 \cdot 10^{-3}$

It is obvious that the sample with Nickel is more resistant to corrosion because it forms a sparingly soluble product, the mixed phosphate of Zn(II), Fe(II) și Ni(II), in stable oxidation states, which allows the formation of an uniform and compact layer, adherent to the substrate, with well-developed in volume dendrites. The Hexamethylene tetramine, as surface agent, through its ability of high dispersion and irrigation, provides a thick, uniform and compact layer, with well-developed dendrites, hence the good corrosion resistance. Referring to the phosphates of Zn(II) and Fe(II) containing Mg(II) and Co(II), we can say that they have a poor corrosion resistance, which is because these induce layer permeability to oxidizing agents. Moreover, Co(II) is likely to form unstable structures, as the presence of nitrate ion allows partial transition of Co(II) to Co(III), which is photosensitive.

4. Conclusions

From the structure morphology and the corrosion data, in table 3 we can conclude that:

- sample X3 (with Ni(II)) has the best corrosion resistance and S1 (zinc phosphate with cobalt chloride) the lowest.
- From the cyclic voltammogram of X5 (with hexamethylene tetramine) we can see that in a short time from immersion (12h) the corrosion resistance drops (from 108420Ω to 3272.9Ω).
- X1_d sample (which was degreased and pickled) has a very low corrosion resistance, because the phosphate layer was removed during the pickling.
- X3 forms a sparingly soluble product, of the mixed phosphate of Zn(II), Fe(II) and Ni(II), in very stable oxidation states, allowing the formation of an uniform and compact layer, adherent to the substrate, but also the formation of some well-developed 3D dendrites.
- On X5 (with hexamethylene tetramine) we can observe the formation of an uniform and compact layer and of much thicker dendrites.
- The layers containing Mg and Co have poor corrosion resistance because the phosphates are permeable to the oxidizing agents, the layers being uneven. Moreover, Co(II) is likely to form unstable and photosensitive compounds (Co(II,III)).
- All the resulted data are very well correlated to the morphology of the layers.

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References

- [1] E. I. Ghali, R.J.A. Potvin, *Corrosion Science* **12**, 583 (1972).
- [2] I. M Zin, S. B. Lyon, V. I. Pokhmurskii, M.C. Simmonds, *Corros. Eng. Sci. Technol.*, **39**, 167 (2004).
- [3] A. Marinescu, Gh. Andonianț, E. Bay, *Electrochemical and Chemical Technologies of Protection of Metallic Materials*, Ed. Tehnica, Bucuresti, 1984.
- [4] H.E. Townsend, NACE Annual Corrosion Conference, Cincinnati, OH, Paper 416, 1991.
- [5] L. Oniciu, E. Grüwald. *Galvanotechnica*, Ed. Științifică și Enciclopedică, Bucuresti, 1980.
- [6] W. Rausch, *The Phosphating of Metals*, Finishing Publications Ltd. (UK), 1990.
- [7] K. Ogle, A. Tomandl, N. Meddahi and M. Wolpers: *Corrosion Science*, **46**, 979 (2004).
- [8] M. Sabouri, T. Shahrabi, H. R. Faridi, M. Salasi: *Corros. Eng. Sci. Technol.*, **44**, 51 (2009).
- [9] N. Etteyeb, M. Sanchez, L. Dhouibi, C. Alonso, C. Andrade, E. Triki, *Corros. Eng. Sci. Technol.*, **41**, 336 (2006).
- [10] N. Satoh, T. Minami, *Surface and Coatings Technology*, **34**, 331 (1988).
- [11] A.V. Sandu, C. Coddet, C. Bejinariu, *Revista de Chimie*, **63**, 311 (2012).
- [12] A.V. Sandu, C. Bejinariu, A. Predescu, I.G. Sandu, C. Baci, I. Sandu, *Recent Patents on Corrosion Science*, **1**, 33 (2011).
- [13] J.F. Gu, Bingyan, *J. Optoelectron. Adv. Mater.* **10**, 405 (2008).
- [14] F. Fang, J.H. Jiang, S.Y. Tan, A.B. Ma, J.Q. Jiang, *Surface & Coatings Technology*, **204**, 2381 (2010).
- [15] M. Sheng, Y. Wang, Q. Zhong, H. Wu, Q. Zhou, H. Lin, *Surface & Coatings Technology* **205**, 3455 (2011).
- [16] B. Narayanasamy, A.J. Amalraj, J.A. Selvi, S. Rajendran, *Bulletin of Electrochemistry*, **21**, 489 (2005).
- [17] J. Creus, H. Mazille, H. Idrissi, *Surface and Coatings Technology*, **130**, 224 (2000).
- [18] C. Bejinariu, I. Sandu, A. Predescu, I.G. Sandu, C. Baci, A.V. Sandu, *Bulletin of the Polytechnic Institute of Iași, Section Material Science and Engineering, LV (LIX)*, **1**, 73 (2009).
- [19] A.V. Sandu, C. Bejinariu C., *Bulletin of the Polytechnic Institute of Iași, Section Material Science and Engineering, Tom LVI (LX)*, **2**, 113 (2010).
- [20] A.V. Sandu, C. Bejinariu C., *Bulletin of the Polytechnic Institute of Iași, Section Material Science and Engineering, Tom LVI (LX)*, **4**, 97 (2010).
- [21] C. Bejinariu, I. Sandu, V. Vasilache, I.G. Sandu, M.G. Bejinariu, A.V. Sandu, M. Sohaci, V. Vasilache, Patent RO125456-A2/2010-05-28.
- [22] C. Bejinariu, I. Sandu, C. Predescu, V. Vasilache, C. Munteanu, A.V. Sandu, V. Vasilache, I.G. Sandu, Patent RO125457-A2/2010-05-28.
- [23] A.V. Sandu, C. Coddet, C. Bejinariu, *J. Optoelectron. Adv. Mater.* **14**, 699 (2012).
- [24] V.I. Trusov, V.L. Kiselev, Patent RU2241069 (C2)/2004.
- [25] N.V. Varentsova, V.A. Chumaevsij, Patent RU2111282 (C1)/1998.
- [26] G. Nemțoi, M. S. Secula, I. Crețescu, S. Petrescu: *Revista de Chimie*, **58**, 2007, 1216-1220.
- [27] S. Petrescu, M. S. Secula, G. Nemtoi, I. Cretescu, *Revista de Chimie*, **60**, 462 (2009).
- [28] M. Sánchez, J. Gegori, M. C. Alonso, J. J. Garcia-Jareno, F. Vicente, *Electrochimica Acta*, **52**, 47 (2006).
- [29] S. Ningshen, U.K. Mudali, G. Amarendra and B. Rai: *Corrosion Science*, **51**, 322 (2009).
- [30] J. O'M. Bockris and A.K.N. Reddz, *Modern Electrochemistry*, 2nd edn, New York, Plenum Press, 1970.

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