

**Second Regional Symposium  
on Electrochemistry  
South-East Europe**

**PROCEEDINGS**



**Belgrade, Serbia, June 6-10, 2010.**

CIP - Каталогизacija у публикацији  
Народна библиотека Србије, Београд

621.357/.359(082)(0.034.2)  
541.1(082)(0.034.2)  
620.193/.197(082)(0.034.2)  
66.087(082)(0.034.2)  
543.25(082)(0.034.2)

REGIONAL Symposium on Electrochemistry South-East Europe  
(2 ; 2010 ; Beograd) Proceedings [Elektronski izvor] / Second  
Regional Symposium on Electrochemistry South-East Europe,  
RSE-SEE, Belgrade, Serbia, June 6-10, 2010. ; [editors Branislav  
Nikolić, Vesna Mišković-Stanković, Aleksandar Dekanski]. – Belgrade :  
Serbian Chemical Society, 2010 (Belgrade : Serbian Chemical Society).  
- 1 elektronski optički disk (CD-ROM) : tekst ; 12 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovnog ekrana. –  
Tiraž 270. - Bibliografija uz svaki rad.

ISBN 978-86-7132-044-3

a) Електрохемијско инжењерство - Апстракти b) Галванотехника –  
Апстракти c) Електрохемија – Апстракти d) Електрохемијске  
реакције - Апстракти e) Антикорозиона заштита - Апстракти  
f) Аналитичка електрохемија - Апстракти  
COBISS.SR-ID 175354892

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Published by

**Serbian Chemical Society**, Karnegijeva 4/III, PAK 135804, 11120 Belgrade, **SERBIA**  
phone./fax: +381 11 3370 467; [www.shd.org.rs](http://www.shd.org.rs), E-mail: [Office@shd.org.rs](mailto:Office@shd.org.rs)

For Publisher

**Ivanka POPOVIĆ**, *President of the Society*

Editors

**Branislav NIKOLIĆ**

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**Aleksandar DEKANSKI**

Cover Design, Page Making and Computer Layout

**Aleksandar DEKANSKI**

Circulation:

**270 Copy Printing**

ISBN **978-86-7132-044-3**

Copying

**Serbian Chemical Society** - Karnegijeva 4/III, Belgrade, **SERBIA**

## The study of the iron phosphate coating porosity in buffered borate solution

Jovan P. Popić, Bore Jegdić\*, Jelena B. Bajat\*\*, Vesna Mišković-Stanković\*\*

*ICTM-Department of Electrochemistry, University of Belgrade, Njegoševa 12, Belgrade, Serbia*

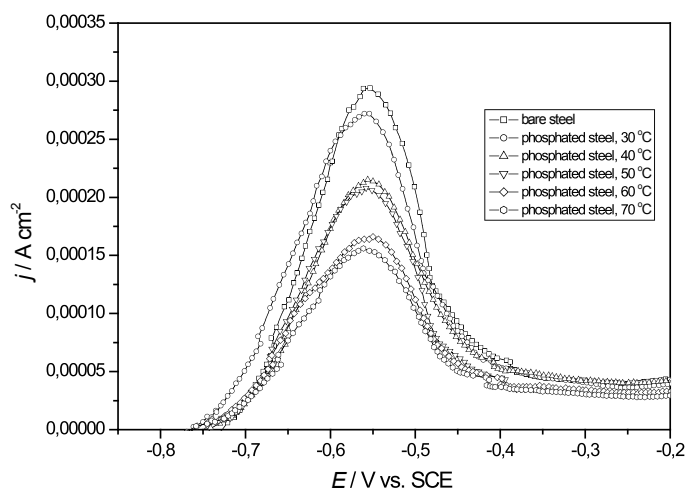
*\*Institute Goša, Milana Rakića 35, Belgrade, Serbia*

*\*\*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade, Serbia*

The iron phosphate layer on the low carbon steel surface slows steel corrosion in aggressive environments. The quality of the iron phosphate layer depends on the fraction of the total surface area covered by phosphate coating. Various factors affect this coverage fraction, in particular the composition of the deposition bath, bath temperature, deposition time, the morphology of the deposit and additives used in the electrolyte<sup>1,2</sup>.

The samples used in this study were low carbon steel. Prior to deposition of phosphate coatings, steel surface was degreased and mechanically polished with 600-grade emery paper and rinsed with distilled water. Phosphating was carried in the phosphate solution (NaOH + H<sub>3</sub>PO<sub>4</sub> + NaNO<sub>2</sub>, pH 3,8) at different temperatures (30-70°C), during 5-15 min. The porosity of phosphate coating on low carbon steel was determined using electrochemical voltammetric anodic dissolution technique (VAD)<sup>3,4</sup> in borate solution. The morphology of phosphate coating on steel was studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Anodic polarization curves (VAD technique) for bare steel and steel with phosphate coatings in borate solution are shown in Fig. 1. The phosphate coating deposited on the steel surface decreased the anodic dissolution rate of steel, as well as reduced the anodic current passivation peaks. The increase of the temperature of phosphate solution resulted with coatings that decreased anodic dissolution of steel.



*Fig 1. Anodic polarization curves for bare steel and phosphated steel at different temperatures, in the buffered borate solution; pH 7.6,  $v = 2 \text{ mV s}^{-1}$ .*

A comparison of the passivation charge density of the bare substrate (standard passivation charge density,  $Q_{\text{pass}}^0$ ) and that of the coated substrate ( $Q_{\text{pass}}$ ) provides values of the coating porosity (Eq. 1).

$$\Theta = Q_{\text{pass}} / Q_{\text{pass}}^0 \quad (1)$$

The charge density used to calculate the porosity corresponds to the area under the curve up to the passivation peak (Fig. 1) and the results obtained for bare steel and phosphated steel deposited at different temperatures of the phosphate solution are shown in Table 1.

Table 1. Values of passivation charge density,  $Q_{pass}$ , and the porosity,  $\theta$ , for bare steel and phosphated steel deposited at different temperatures of the phosphate solution during 5 min

Substrate	$Q_{pass}$ , mC cm <sup>-2</sup>	$\theta$ , %
Bare steel	12.26	100
Phosphate coating, 30 °C	12.12	99.1
Phosphate coating, 40 °C	9.01	73.7
Phosphate coating, 50 °C	9.14	73.7
Phosphate coating, 60 °C	8.15	65.9
Phosphate coating, 70 °C	6.87	56.6

The porosity values for phosphate coatings on steel deposited during different time, at 50°C, are shown in Table 2.

Table 2. Values of passivation charge density,  $Q_{pass}$ , and the porosity,  $\theta$ , for bare steel and phosphated steel deposited during different time period

Substrate	$Q_{pass}$ , mC cm <sup>-2</sup>	$\theta$ , %
Bare steel	12.26	100
Phosphate coating, 50°C, 5 min	9.14	73.7
Phosphate coating, 50°C, 10 min	7.58	61.8
Phosphate coating, 50°C, 15 min	7.26	59.2

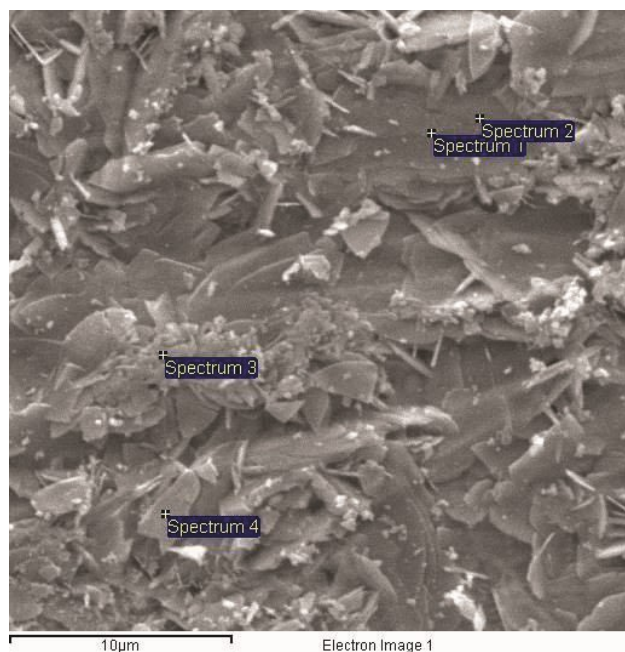
On the basis of the results presented in Fig. 1 and Tabs. 1 and 2 we can conclude that porosity of the phosphate coatings depends on the temperature of the phosphate solution and deposition time. The increases of the temperature of the phosphate solution, as well as of the deposition time, decrease the porosity of phosphate coating on steel. The lowest porosity was obtained for phosphate coating deposited at 70°C, during 5 min.

The addition of NaNO<sub>2</sub> in the phosphate solution significantly decreased phosphate coating porosity. Different amounts of NaNO<sub>2</sub> in the phosphate solution were tested (0.1 – 1.0 g dm<sup>-3</sup> NaNO<sub>2</sub>) for different solution temperatures and the lowest porosity of phosphate coating (35.1%), was obtained with 1.0 g dm<sup>-3</sup> NaNO<sub>2</sub> in the phosphate solution, at 50°C, during 5 min (Table 3).

Table 3. Values of passivation charge density,  $Q_{pass}$ , and the porosity,  $\theta$ , for bare steel and phosphated steel deposited with different concentration NaNO<sub>2</sub> in the phosphate solution.

Substrate	$Q_{pass}$ , mC cm <sup>-2</sup>	$\theta$ , %
Bare steel	12.26	100
Phosphate coating, 50°C	9.14	73.7
Phosphate coating, 50°C + 0,1 g dm <sup>-3</sup> NaNO <sub>2</sub>	5.52	44.7
Phosphate coating, 50°C + 0,5 g dm <sup>-3</sup> NaNO <sub>2</sub>	5.01	40.5
Phosphate coating, 50°C + 1,0 g dm <sup>-3</sup> NaNO <sub>2</sub>	4.35	35.1

The morphology of the phosphate coating deposited from the phosphate solution with 0.5 g dm<sup>-3</sup> NaNO<sub>2</sub> ( $\theta$  =40.5), at 50°C, during 5 min, is shown in Fig. 2. The study of the phosphate coating morphology showed that coating was evenly deposited on the whole steel surface. There are two characteristic forms of phosphate coating: laminated structure and needle-like forms. The EDS measurements provided the information of the concentration of particular elements on the phosphate coating surface. On the basis of the results of four independent measurements, taken on different surface spots, the average value for the concentration of the elements was calculated: oxygen 37.6%, phosphor 3.26% and iron 59.14%. Assuming that phosphate coating was made of iron phosphate FePO<sub>4</sub> and iron oxide Fe<sub>2</sub>O<sub>3</sub>, it could be proposed that phosphate coating contains 17.6% FePO<sub>4</sub> and 82.4% Fe<sub>2</sub>O<sub>3</sub>.



Spectrum	O	P	Fe	FePO <sub>4</sub>	Fe <sub>2</sub> O <sub>3</sub>
Spectrum 1	22.14	1.46	76.40	7.9	92.1
Spectrum 2	27.15	1.72	71.14	9.3	90.7
Spectrum 3	50.61	5.18	44.21	28.0	72.0
Spectrum 4	50.50	4.68	44.82	25.3	74.7
Mean	37.60	3.26	59.14	17.6	82.4

Fig 2. Surface morphology (SEM) of phosphate coating deposited on steel from the phosphate solution with 0.5 g dm<sup>-3</sup> NaNO<sub>2</sub>, during 5 min at 50°C and the EDS spectrums corresponding to particular surface spots.

On the basis of the cross section analysis of the coating surface, acquired with AFM technique (Fig.3) it was shown that the grain height is 2 μm, whereas the width ranges from 2 to 5 μm.

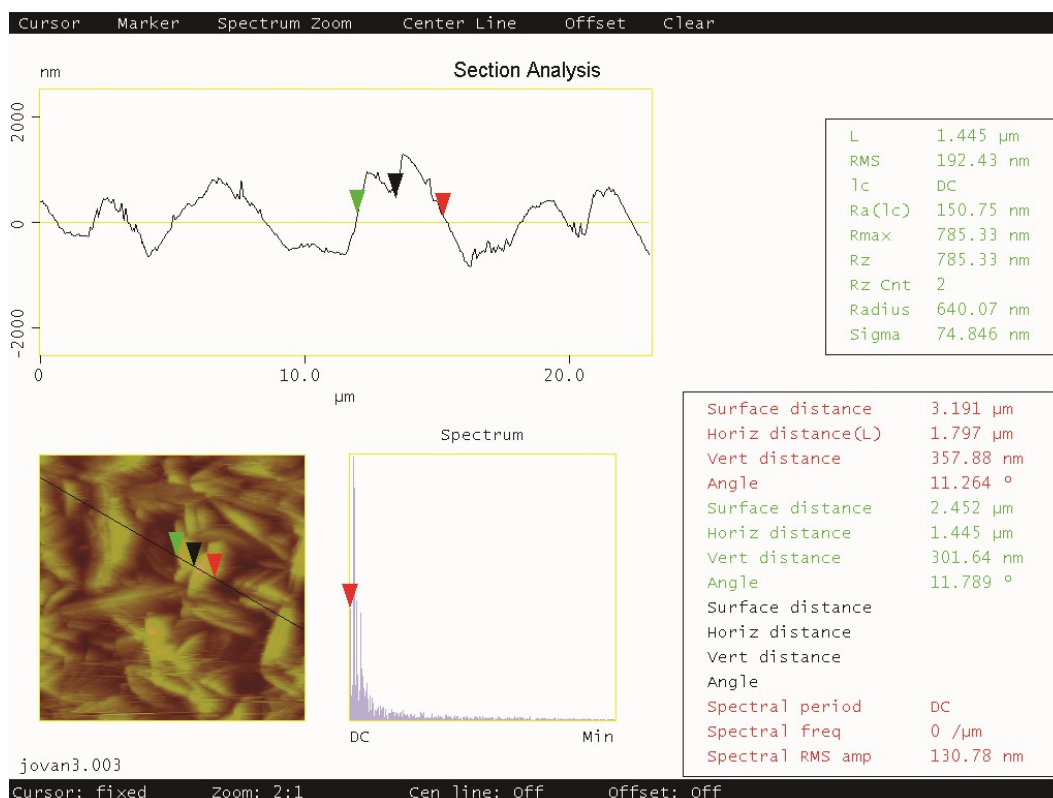


Fig.3. AFM image of phosphate coating deposited on steel from the phosphate solution with 0.5 g dm<sup>-3</sup> NaNO<sub>2</sub>, during 5 min, at 50°C.

On the basis of all the results presented it could be concluded that porosity of phosphate coatings on the steel is very high. However, the temperature of phosphate solution and the addition of  $\text{NaNO}_2$  in the phosphate solution significantly decrease the porosity of the phosphate coatings. The lowest porosity of the phosphate coating on steel was obtained with  $1.0 \text{ g dm}^{-3}$   $\text{NaNO}_2$  in the phosphate solution, at  $50^\circ\text{C}$ .

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