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The Effect of Surface Mechanical Activation on Protection Properties of Zinc Phosphate Coating

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Abstract: The effect of surface mechanical activation such as grinding of surface by 180 grade emery papers, sand blasting and shot blasting on the quality of zinc phosphate coating is discussed in this paper. The investigation of coating morphology by Scanning Electron Microscope technique shows that a uniform and fine-grained coating formed on the sand blasted surface compared with the non-uniform and coarse coating formed on the grinded and shot blasted surface. Furthermore, the measurements of corrosion resistance through the electrochemical techniques such as polarization and Electrochemical Impedance Spectroscopy show that preparation operation of surface by sand blasting has evident influence on improving protection properties of formed phosphate layer. As well, activation of surface by sandblasting, improves the paint adhesion.

Key words: Plain carbon steel · Mechanical surface activation · Phosphating · Fine-grained coating, protective properties · Paint adhesion

INTRODUCTION

Phosphating is a well-known conversion process that has been widely used in automobile, aerospace and military industries as a surface pretreatment process [1-4] on plain carbon steel [5-7]. Indeed, chemical pretreatment of surface by phosphating operation prior to painting is a key technology to ensure good bonding between paint film and substrate [2, 8]. Because zinc phosphate coating is micro-porous, paint can sink in it [1]. Moreover, the phosphate coating as an electrical insulation, slows metal corrosion in aggressive environments [9, 10] and improves the lubrication properties of the metal surface [11].

The literature [12-15] cites that many factors such as temperature and time of phosphating treatment, the concentration of the ingredients in supersaturated solution, structure and chemical composition of base metal, pretreatment of solution with magnetic fields, ultrasonic irradiation and surface preparation influence morphology, thickness, chemical composition and protective properties of formed phosphate layer.

The purpose of the present paper is to investigate the effect of diverse methods of surface mechanical preparation such as grinding by 180 emery papers, sand blasting and shot blasting on the change of surface state of plain carbon steel and consequently its effect on the microstructure and properties of formed phosphate coating such as corrosion resistance and paint adhesion.

Experimental Procedure: The substrate used in this study is plain carbon steel with dimensions of 80 mm×40 mm×2 mm in size. The surface activation of samples was carried out by three different mechanical methods including grinding by 180 emery papers, sand blasting and shot blasting. The details of surface activation were given in our earlier submitted papers to this journal. After that, the samples were degreased in 10% NaOH solution with temperature of 85°C for 10 min and pickled in 20% HCl. In the next stage, the samples were immersed into a phosphate solution containing 15 ml H_3PO_4 (85%), 10 g/l ZnO, 2 g/l $NaNO_3$ and 4.2 ml HNO_3 (65%) with free acid value (FA) 1.5 point and total acid value (TA) 21 point, for 10 min. The phosphating temperature was 60-65°C. The coverage conditions are given in Table 1.

A comparison between morphology of formed coating on the surface, after its activation by different mechanical methods was performed by SEM (Cam Scan MV2300). Also, the corrosion resistance of samples was compared through the electrochemical measuring techniques. For this purpose, at first the samples were sealed by epoxy resin such a way that their one side with

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Table 1: The coverage conditions applied on the substrate

Substrate ID	Coverage condition
Untreated	Surface without phosphating
G-Ph	Grinding & phosphating
S-Ph	Sand blasting & phosphating
Sh-Ph	Shot blasting & phosphating

area of 1 cm^2 are exposed to 3.5% NaCl solution. Polarization test was carried out with a Potentiostat/Galvanostat (BHP 2061-C Electrochemical Analysis System, Behpajooh, Iran); and after an initial potential stabilization in corroding solution for 10 min at an ambient temperature, the samples were polarized from open circuit potential (OCP) in the cathodic-anodic direction with a scan rate of 0.001 mV s^{-1} and maximum overvoltage about ±250 mV. Furthermore, the EIS measurement was carried out under galvanostatic condition using a potentiostat/galvanostat EG & model parstate 2263 at corrosion potential with amplitude of perturbation signal 10 mV in the frequency range of 0.01 Hz to 10 KHz and the results were analyzed with Zview software for Windows. In all of the electrochemical tests, the three-electrode cells including a saturated calomel electrode as the reference, a platinum electrode with 1cm^2 surface area as the counter electrode and the samples as a working electrode, were used.

Moreover, in order to investigate the paint adhesion, a double layer coat containing epoxy primer with Dry Film Thickness (DFT) of about 45±5 ìm and Polyurethane final coat with Dry Film Thickness (DFT) of about 35±5 ìm was sprayed on the surface, respectively. In this article, the dry adhesion extent of paint was evaluated according to the ASTM D 3359-02 standard, wherein, the quality of adhesion is classified from 0B to 5B. The classification of "0B" indicates the worst adhesion and "5B" indicates the best adhesion result. Also, wet adhesion measurements was performed according to the described method for examining dry adhesion, but after 240 h of immersion of painted samples in distilled water at 45 °C.

RESULTS AND DISCUSSION

The Morphology of Phosphate Coating: SEM micrographs of coatings applied on the activated surfaces of plain carbon steel by various mechanical methods are shown in Fig. 1.

As shown, the activation of surface by sand blasting operation, causes the formation of a uniform fine-grained phosphate coating (Fig.1 a/d), compared to coarse and uneven phosphate layer formed on the grinded surface (Fig.1 b/e) and shot blasted surface (Fig.1 c/f).The details of coating morphology investigation, etc. were given in our earlier submitted papers to this journal.

Electrochemical Tests

Polarization Test: Fig. 2 shows the polarization curves of Sh-Ph, G-Ph, S-Ph and untreated samples. The corrosion current (i_{corr})be measured with the help of Eq. 1:

$$R_p = B / i_{corr} = \Delta E / \Delta I \qquad (1)$$

In the above Eq, B is an empirical polarization resistance constant that can be calculated using the anodic (b_a) and cathodic (b_c) Tafel slopes according to the Eq. 2.

$$B = \left[b_a . b_c / 2.3\left(b_a + b_c\right) \right] \qquad (2)$$

As well, the protection efficiency (η) of coatings are calculated with Eq. 3 [16].

$$\%\eta = \left[1 - \left(i^0_{corr} / i_{corr} \right) \times 100 \right] \qquad (3)$$

Where, i^0_{corr} is the corrosion resistance of untreated sample and i_{corr} is corrosion resistance of phosphated sample. The amounts of coating porosity are calculated through the Eq. 4:

$$F = (R_{p,M} / R_p) \times 10^{-\left|\Delta E_{corr}\right| / b_a} \qquad (4)$$

Where, F is the porosity of phosphate coating, $R_{P,M}$ is the polarization resistance of the untreated sample, R_P is the polarization resistance of phosphated sample, ΔE_{corr} is the difference of E_{corr} between untreated sample and phosphated sample and b_a is the anodic Tafel slope of base metal [17].

The results of these calculations (are listed in Table 2) show the highest corrosion rate for untreated sample and therefore indicate the necessity of its protection. In contrast, with applying phosphate coating, the amount of corrosion rate decreases that can be related to the insulating properties of this coating. Besides, by the formation of the compact and fine-grained coating on the sand blasted surface, corrosion rate decreases much more that can be related to the decreasing of coating porosity.

a) Sand blasting\ phosphating(S-Ph) b) Grinding\ phosphating(G-Ph) c) Shot blasting\ phosphating(Sh-Ph)

Fig. 1: SEM micrographs of phosphate coating applied after preparation of surface by different mechanical methods

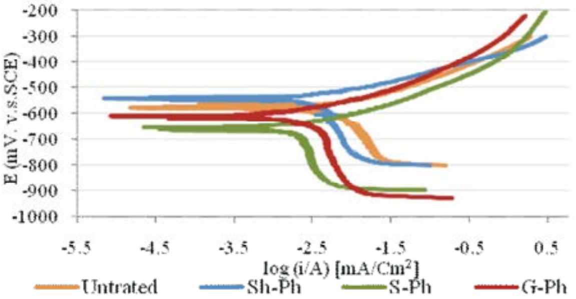


Fig. 2: Polarization curves measured for Sh-Ph, G-Ph, S-Ph and untreated samples in 3.5% NaCl

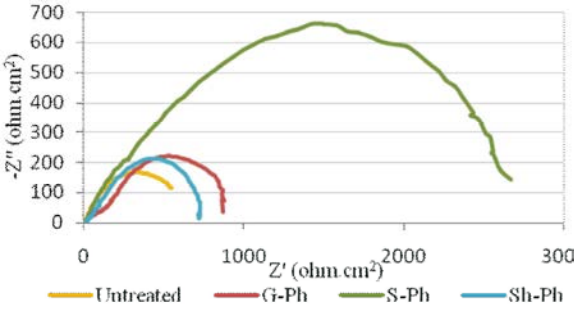


Fig. 3: Nyquist diagrams of samples immersed in 3.5% NaCl sol

Fig. 4: Electrical equivalent circuit for fitting the EIS results

Electrochemical Impedance Spectroscopy Studies: The Nyquist plots of the Sh-Ph, G-Ph, S-Ph and untreated samples are shown in Fig. 3. These plots consist of only one capacitive loop, thus an equivalent circuit model, with one time constant (Fig. 4) is used for their analysis.

Table 2: The obtained results of polarization experiment

	I_{corr} (mA.cm^{-2})	Porosity percentage	Protection efficiency
Untreated	6.096E-3	-	-
Sh-Ph	2.995E-3	6.28	50.87%
G-Ph	2.346E-3	6.44	61.52%
S-Ph	1.347E-3	4.51	77.91%

The EIS data are fitted with a corresponding electrical circuit model using Zview version 2.3f (P.5), where R_s represents the ohmic resistance between reference and working electrodes and R_p represents the polarization resistance of the phosphate coating. For a better fitting and accounting the phenomena related to microscopic roughness and inhomogeneous of surface, a constant-phase element is used in the equivalent instead of a pure capacitance [18]. Its impedance is given by Eq. 5. [18, 19]:

$$F = \left({R_{p,M}}/{R_p} \right) \times 10^{-\left|\Delta E_{corr}\right|/b_a} \tag{5}$$

Where ù is the angular frequency of ac-voltage, Y_0 and n are the frequency independent parameters and CPE represents an ideal capacitor for n=1, a resistor for n=0 and an inductance for n=-1 [18]. Meanwhile, double-layer capacitance, C_{dl}, can be calculated from Eq. 6 [20].

$$C_{dl} = \left[{Y_0}/{\left(R_s^{-1} + R_p^{-1}\right)} \right]^{1/n} \tag{6}$$

These estimated elements of this fitting with errors smaller than 5% are summarized in Table 3.

With regard to the plots (Fig. 3) and the reported results in Table 3, it is indicated that the diameter of the low frequency (LF) capacitive loop and the amount of charge transfer resistance become larger, when phosphate coating is applied on the surface. On the other hand, much more increasing in the charge transfer resistance and diameter of capacitive loop is observes after phosphating of surface sandblasted at the same coverage time (10 min). Therefore, sandblasting operation has the beneficial effect on the formation of compact and fine

Table 3: Electrochemical parameters obtained using the EIS technique

	$R_s(\Omega\cdot cm^2)$	$R_p(\Omega\cdot Cm^2)$	$Y_0(\Omega^{-1}s^{-n})$	CPE-n	$C_{dl}(F/cm^2)$
Untreated	11.48	626.2	3E-1.53	0.71	3E-1.49
Sh-Ph	18.44	898.7	4E-8.41	0.52	4E-6.52
G-Ph	19.98	1249	4E-6.59	0.57	4E-5.69
S-Ph	12.22	2833	4E-2.30	0.62	4E-1.78

Table 4: The results of dry adhesion of paint on the untreated and phosphated samples

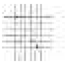
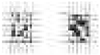
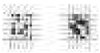
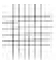
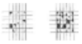
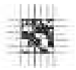
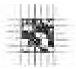
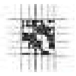
			Classification			
Paint	Final Featue	ASTM D 3359	1st sample	2nd sample	3rd sample	Average classification
Air dry paint (Epoxy-Polyurethane) (about 70 ìm in thickness)	Sand blasted 		4	3	4	4B
	Grinded 		1	2	1	1B
	Shot blasted 		1	1	0	1B
	S-Ph 		5	5	4	5B
	G-Ph 		2	2	3	B
	Sh-Ph 		2	2	2	2B

Table 5: The results of wet adhesion of paint on the untreated, phosphated samples

			Classification			
Paint	Final Feature	ASTM D 3359	1st sample	2nd sample	3rd sample	Average classification
Air dry paint (Epoxy-Polyurethane) (about 70 ìm in thickness)	Sand blasted 		0	0	0	0B
	Grinded 		0	0	1	0B
	Shot blasted 		0	0	0	0B
	S-Ph 		3	3	2	3B
	G-Ph 		1	1	1	1B
	Sh-Ph 		1	1	1	1B

grained coating with higher corrosion resistance compared with other preparation methods of surface such as grinding and shot blasting, supporting the previous presented results.

Influence of Phosphate Coatings on Paint Adhesion: The results of dry adhesion, shown in Table 4, reveals that, with sand blasting due to creating a surface with suitable roughness, the adhesion of paint film is increased. Indeed, the surface roughness causes the better mechanical bonding between substrate and paint film. But the over increasing of surface roughness by shot blasting operation, damages the paint film and the quality of adhesion decreases. As well, with applying the phosphate coating with micro-porous structure the paint adhesion improves. At this case, formation of fine-grained coating with higher coverage on sandblasted surface increases the paint adhesion more than phosphate layer applied on the grinded or shot blasted surface. The coating applied on shot blasted or grinded surface is uneven due to having very coarse crystallites that causes the poor adhesion of paint and these coarse crystallites damage the paint film. Also, the results of wet adhesion are listed in Table 5. Investigations showed that after 240 h exposure of uncoated samples, due to high permeability of the paint film and corrosion of untreated substrate, the quality of adhesion drops. But, with applying the insulate phosphate layer, due to decreasing corrosion under paint film, the wet adhesion of paint improved. Also, as can be seen, with the formation of the more compact and fine grained coating on the sandblasted surface, the wet adhesion showed the further increasing.

CONCLUSION

This paper addresses a study on the effect of surface activation by diverse mechanical methods on the characterization of formed phosphate layer. The results show that mechanical activation methods with changing surface state affect the number of nucleuses and final size of phosphate crystallites. So that activation of surface by sand blasting operation produces a coating with fine grain size phosphate crystallites than formed layers on the shot blasted and grinded surface. As well, the results of protective properties investigation such as salt spray, polarization and EIS show that formation of fine-grained and compact coating on the sand blasted surface, significantly improves corrosion resistance of sample. Moreover, the results of dry adhesion reveals that with sand blasting, because of creating a surface with suitable roughness for better mechanical bonding between substrate and paint film, the adhesion of paint film increases. But the over increasing of surface roughness, by shot blasting operation, damages the paint film. As well, with applying the phosphate coating with micro-porous structure, the paint adhesion is improved. At this case, formation of fine-grained coating with higher coverage on sandblasted surface further increases the paint adhesion. Also, the results of wet adhesion show that the uniform and compact coating applied on the sandblasted surface, due to increasing corrosion resistance of sample under the paint film, increases the wet adhesion compared with formed layer on the grinded or shot blasted surface.

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