



Rapid Electrochemical Phosphating at Room Temperature†

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The application of electrochemical method in phosphating treatment accelerates ion diffusion at room temperature. By applying this method the process can be completed within 10 min. After careful screening, the crystalline phosphate film exhibited the best comprehensive performance, under the condition where manganous dihydrogen phosphate concentration was 30-50 g/L, zinc nitrate concentration was 50-70 g/L, current density was 1.00-1.50 A dm⁻² and electrochemical phosphorization time was 5-7 min at room temperature. In addition, the analytical studies indicated that the strong corrosion resistant phosphate film, which mainly contains O, Zn, P, Mn and Fe, is uniform compact and easy for the coat to adhere.

Keywords: Phosphating, Electrochemical method, Scanning electron microscopy, Surface treatment.

INTRODUCTION

Generally, to improve the adhesion between metal matrix and coating and enhance the corrosion-resistant ability, the metal matrix is treated with an effective surface treatment. Phosphating is one of the most common pretreatment technologies and it has been widely used in chemical engineering, automobile, pharmaceutical, water treatment and other industries¹⁻⁷. The metal matrix is immersed in a phosphate solution, where a uniform phosphate protective film is formed on the surface chemically. The phosphate film can form at all high, medium or low temperature. The low temperature phosphating processes have become more significant today due to the escalating energy costs since 1940s⁸. However, low temperature phosphating processes are still slowly and should be accelerated by some means. Electrochemical means of acceleration has been studied by previous workers⁹⁻¹⁸, but even so the low temperature phosphating processes generally need more than 10 min. A better phosphate film can be acquired at medium temperature but with several drawbacks including high energy consumption, unknown solution composition, non-uniform film, corrosion and hydrogen embrittlement. Moreover, highly toxic hexavalent chromium is always added to fix the 0.5-1.5 % pores on the surface of metal matrix after traditional treatment and amine or sodium nitrobenzene sulphonate (SNBS), which are environmentally hazardous, is needed to enhance the chemical reaction rate.

As a result, it's highly desirable to develop a technology that is environmental-friendly, rapid and easy for the production of highly corrosion-resistant, rigid and fine crystallized phosphate film. In this paper, an electrochemical method is introduced to help ions diffuse faster in phosphate solution and form a stable, dense and insoluble phosphate film on the surface of metal matrix at room temperature.

EXPERIMENTAL

The materials and instruments used in this study included manganous dihydrogen phosphate [Mn(H₂PO₄)₂·4H₂O, chemical pure], zinc nitrate (analytical pure), citric acid (analytical pure), an electronic balance (FA1004), thermostatic water bath (HWS24), direct-current power (JWL-30I), electrochemical workstation (PARSTAT2273), SEM (JSM-6360LV), Falcon EDAX and carbon steel (size: 30 mm × 20 mm × 2mm).

Electrochemical phosphorization treatment

Sample preparation: Carbon steel rust removal → cold water washing → degreasing → hot water washing → cold water washing → acid washing → cold water washing → 0.2 % Na₂CO₃ neutralizing → cold water washing → HCl activation → phosphorization → hot water washing → cold water washing → drying.

Preparation of phosphate solution: 80-100 g zinc nitrate was fully dissolved in 200 mL deionized water and put into a phosphate bath. 30-40 g Mn(H₂PO₄)₂·4H₂O was dissolved into

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500 mL deionized water preheated 60-70 °C. After heated at 80 °C for 10 min, the clear solution was put into the phosphate bath. 2 g citric acid was added to the phosphate bath and the mixture was diluted to 1000 mL.

Electrochemical phosphorization: The pretreated sample of carbon matrix was put into the electrochemical phosphate bath and connected to the cathode of the power. A graphite electrode acted as an anode. Different current densities and reaction times were applied to find the optimal condition for electrochemical phosphorization treatment.

Electrochemical phosphate film property test (A): A 10-point scale was used to evaluate the phosphate film as excellent (10 points), good (9 points), average (8 points) or others (7 points).

CuSO₄ titration test (B): The corrosion resistance of the phosphate film was tested by CuSO₄ titration examination. The CuSO₄ titrant contains 40 g/L CuSO₄·5H₂O, 32 g/L NaCl, 10 mL/L HCl (0.1 mol/L) and distilled water. The phosphate film was cleaned by anhydrous ethanol and dried before the test. CuSO₄ titration solution was then dropped on it and the time it took for the solution colour to change from blue to light red was recorded by seconds.

NaCl immersion test (C): A phosphate sample was immersed in 3 % NaCl solution for 1 h and then put outdoor. The time before the appearance of rust spots on the sample was recorded by days.

Film weight test (W): 50 g/L chromium trioxide was used as the film remover solution. The phosphate weight per unit area *W* was calculated by formula (1) and the unit was g/m²:

$$W = \frac{10 \times (M_2 - M_1)}{S} \quad (1)$$

where *M*₂ is the weight of the sample after phosphorization (g), *M*₁ is the weight of the sample after the film was removed (g) and *S* is the surface area of the sample (m²).

Comprehensive evaluation (M): The comprehensive evaluation *M* was calculated with the four parameters mentioned above with formula (2):

$$M = A \times 10 \% + B \times 10 \% + C \times 10 \% + W \times 70 \% \quad (2)$$

The bigger value of *M* implies better performance of the electrochemical phosphate film.

RESULTS AND DISCUSSION

Concentration of manganous dihydrogen phosphate:

Manganous dihydrogen phosphate [Mn(H₂PO₄)₂] is the major filmogen of zinc and manganous series phosphate film. It contributes Mn²⁺ and H₂PO₄⁻ and accounts for the total acidity. Thus its concentration range should be under precise and appropriate control. The relationship between the acidity of the solution and the amount of manganous dihydrogen phosphate was studied. Manganous dihydrogen phosphate was added to a 50 g/L Zn(NO₃)₂ solution and the acidity of the solution was measured. The acid ratio increases when the concentration of Mn(H₂PO₄)₂ increases (Fig. 1). However, when the salt concentration is too high, the high acid ratio will push the hydrolysis equilibrium of manganous dihydrogen phosphate to the right side, resulting in the higher free acidity and smaller acid ratio.

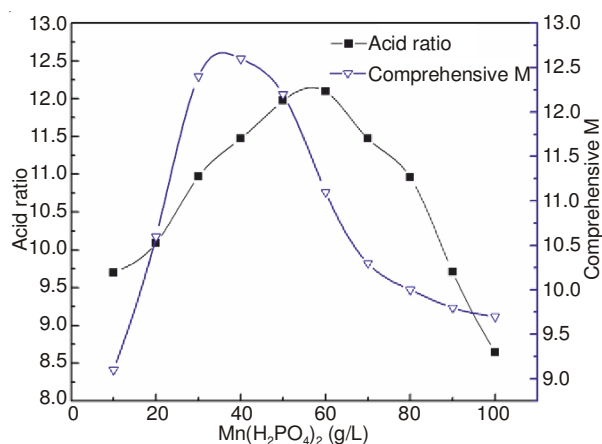


Fig. 1. Influence of Mn(H₂PO₄)₂ on acid ratio and comprehensive M



An overly low concentration of manganous dihydrogen phosphate will result in a poor phosphorization ability and the amount of effective component will decrease rapidly in the phosphorization reaction. The obtained phosphate film will be thin, incomplete, easily removed and with poor corrosion resistance and a low comprehensive M value. However, an overly high level of manganous dihydrogen phosphate concentration will lead to low comprehensive M as well, while resulting in thick, rough and poorly adhesive phosphate film. Therefore, a good phosphate film with high M value will be obtained with a manganous dihydrogen phosphate concentration of 30-50 g/L.

Concentration of zinc nitrate: The influence of zinc nitrate concentration on the acid ratio was examined with the concentration of manganous dihydrogen phosphate at 40 g/L. Fig. 2 showed that when the amount of zinc nitrate was increasing, the value of acid ratio fluctuated. With a certain amount of zinc nitrate in the solution, the acid ratio remained stable. In general, the concentration of zinc nitrate has great influence on the total acidity and acid ratio of the phosphate solution, yet excessive zinc nitrate has limited influence on the acid ratio because of its solubility.

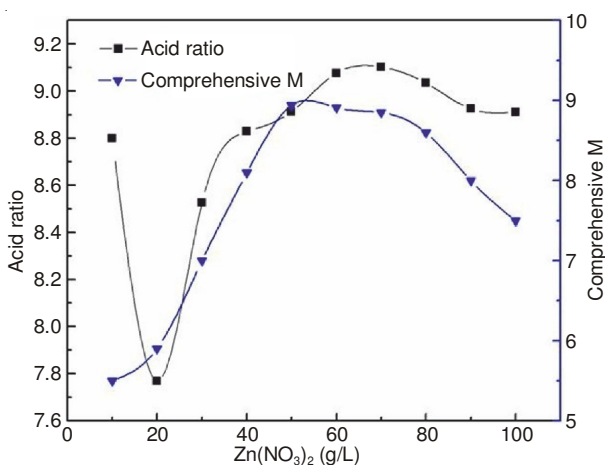


Fig. 2. Influence of Zn(NO₃)₂ on the acid ratio and comprehensive M

The phosphate film formed incompletely with little amount of zinc nitrate. It had poor corrosion resistance and

matrix combination and a low comprehensive M value. On the other hand, with excess amount of zinc nitrate, a rough and thick film with poor corrosion resistance formed. Only certain amount of Zn²⁺, in the range of 50-70 g/L, will help to form uniform, compact, corrosion-resistant phosphate film with high M value.

Electrochemical phosphate current density: The relationship between the current density and the electrochemical phosphate film is shown in Table-1 and Fig. 3. When the current density increases from 0.25 to 5.00 A dm⁻², the phosphate film becomes heavier and both the CuSO₄ titration and immersion time increases first and then decreases. Only thin, incomplete phosphate film with poor corrosion resistance can be formed at very low current density. In contrast, an overly high current density leads to thick and black film with poor corrosion resistance and low comprehensive performance. Moreover, the edge of the phosphate film will be partially burned by current edge effects at high current density. In conclusion, the phosphate film shows better appearance and optimal corrosion resistant ability when the current density is 1.00-1.50 A dm⁻².

Current intensity (A dm ⁻²)	Appearance (point)	Film weight (g m ⁻²)	CuSO ₄ titration time (s)	Immersion time (d)
0.25	7	1.137	18	0.5
0.50	7	3.726	47	0.5
0.75	8	4.458	79	1.0
1.00	9	6.642	124	5.0
1.25	9	8.181	143	5.0
1.50	10	9.435	135	3.0
2.00	8	10.014	102	2.0
3.00	8	10.551	76	3.0
4.00	7	11.624	83	1.0
5.00	7	13.329	31	1.0

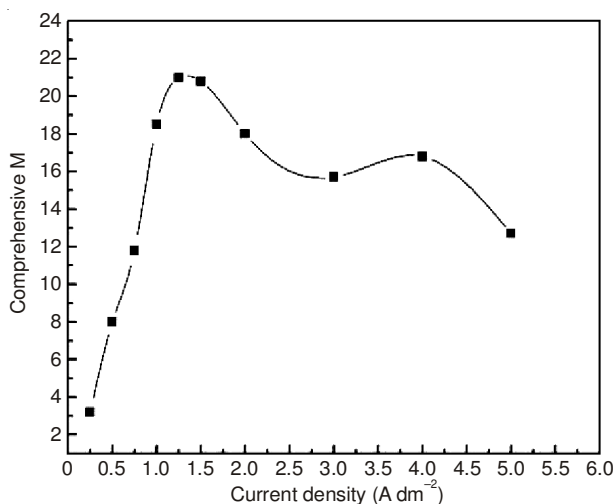


Fig. 3. Relationship between current density and comprehensive M

Electrochemical phosphating time: The influence of different phosphate time on the electrochemical phosphate film and its comprehensive value M is summarized in Table-2.

Longer phosphate reaction processes lead to heavier the phosphate films with smaller pore ratios. The CuSO₄ titration

Phosphate time (min)	Appearance (point)	Film weight ((g m ⁻²)	CuSO ₄ titration time (s)	Immersion time (d)
0.5	7	1.134	15	0.5
1.0	7	1.543	18	0.5
1.5	7	2.346	23	0.5
2.0	7	3.141	47	1.0
2.5	7	3.735	73	1.0
3.0	8	4.091	92	2.0
3.5	8	4.537	86	3.0
4.0	8	5.269	118	3.0
4.5	9	5.736	92	5.0
5.0	9	6.315	134	5.0
6.0	9	6.642	124	6.0
7.0	8	7.548	115	4.0
8.0	8	8.912	106	3.0
9.0	7	10.562	81	2.0
10.0	7	12.743	42	3.0

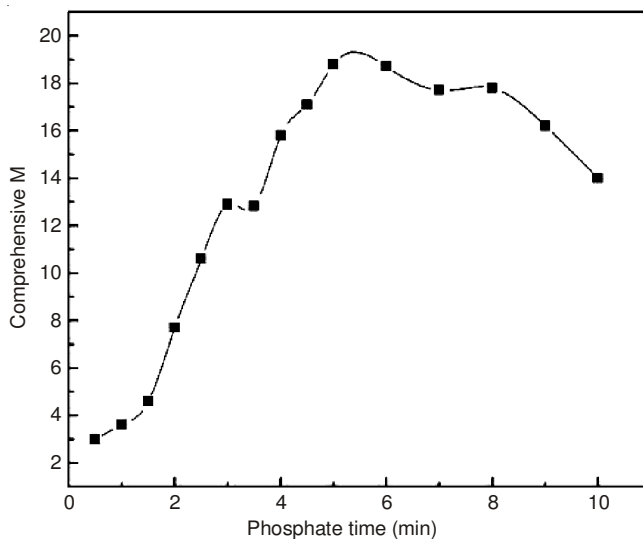


Fig. 4. Relationship between phosphating time and comprehensive M

time first increases and then decreases with the prolonging process. The phosphate film exhibits the best performance only under appropriate phosphate reaction time, for example 5-7 min (Fig. 4).

Corrosion resistant test: Corrosion resistant tests were performed to phosphate films formed with different reaction times at optimal current density, using electrochemical workstation PARSTAT2273, which has SCE as the reference electrode, platinum as the counter electrode, phosphate layer in 1 cm² areas as the working electrode and the rest sealed with silica gel. All the tests were performed in 3.5 % NaCl solution with 2 mV/s scan speed at room temperature. Tafel curves are shown in Fig. 5 and the calculated electrochemical parameters for phosphate film are given in Table-3.

The self-corrosion potential of electrochemical phosphate film tends to be more positive when the reaction starts. After a while, it starts to move to the negative site, indicating that longer reaction time helps to form stronger corrosion-resistant films. In addition, the smallest self-corrosion potential of electrochemical phosphate film was obtained with the reaction

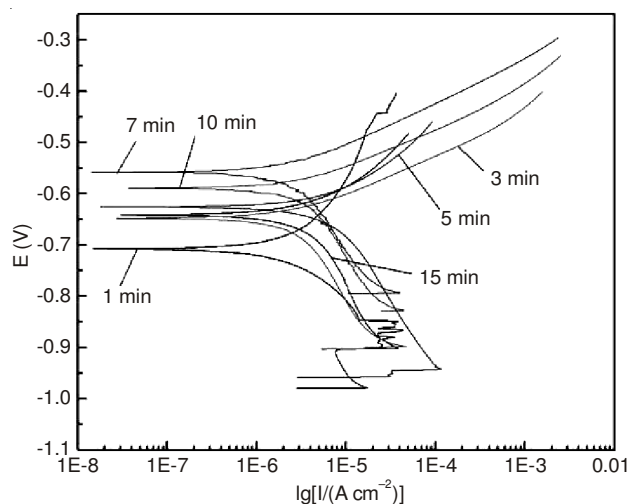


Fig. 5. Tafel curves for the phosphate film

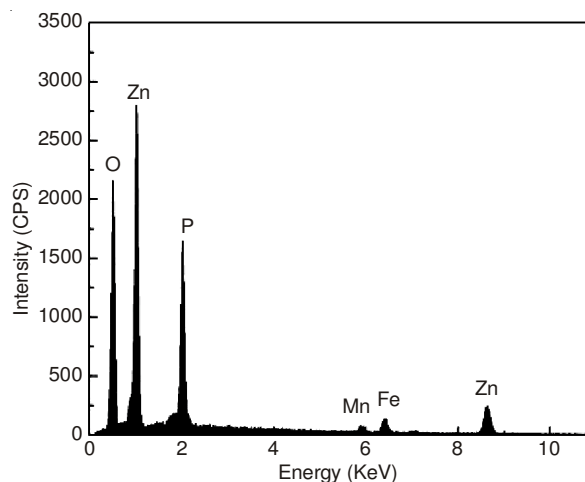


Fig. 7. EDS spectroscopy of phosphate films

TABLE-3
CALCULATED ELECTROCHEMICAL
PARAMETERS FOR PHOSPHATE FILM

Phosphate time (min)	E_{corr} (mV)	I_{corr} (mA/cm ²)
1	-707.86	0.006880
3	-648.23	0.010034
5	-626.62	0.005301
7	-558.40	0.002231
10	-589.27	0.002866
15	-645.94	0.008385

time of 5-10 min, proving that the reasonable reaction time should be 5-7 min.

Appearance and composition: All the phosphate films are well crystallized and radiating out with sheet or clumpy bases as shown in Fig. 6. The films were compact and uniform, making it easy for the coating materials to adhere to them.

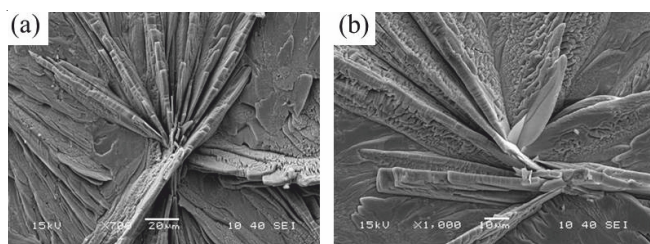


Fig. 6. SEM images of the phosphate films for 700 × (a) and 1000 × (b) magnification

The EDS spectroscopy of the phosphate films and its data analysis are shown in Fig. 7 and Table-4. It can be summarized that the phosphate films mainly consisted of O, Zn, P, Mn and Fe and the weight percentage of Zn was as high as 46.95 %, indicating that the electrochemical phosphate film were crystallized from manganese zinc phosphate or manganese ion phosphate complexes.

Conclusion

Phosphate film exhibits the best comprehensive performance with manganous dihydrogen phosphate concentration of 30-50 g/L, zinc nitrate concentration of 50-70 g/L, current density of 1.00-1.50 A dm⁻² and electrochemical phosphorization time of 5-7 min at room temperature. In addition, this

TABLE-4
EDS DATA ANALYSIS

Element		Wt (%)	At (%)
O	K	27.51	54.81
P	K	16.78	17.27
Mn	K	2.43	1.41
Fe	K	6.33	3.62
Zn	K	46.95	22.90
Total		100	100

crystalline phosphate film is uniform, compact and easily adhered to by the coating. It mainly contains O, Zn, P, Mn and Fe and the weight percentage of Zn compound is as high as 46.95 %.

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