A Zinc and Manganese Phosphate Coating on Automobile Iron Castings


Key Laboratory of Automobile Materials, Ministry of Education, College of Materials Science and Engineering, Jilin University, Nanling Campus, Changchun, 130025, China. E-mail: lianjs@jlu.edu.cn

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A modified phosphate coating on automobile iron castings was described in this paper. The phosphating bath was modified by adding sodium molybdate. The microstructure of the phosphate coating was remarkable refined as the addition of Na$_2$MoO$_4$ increases to 1.5–2.0 g/L. As a result, the corrosion current of the coatings measured by electrochemical polarization decreases as Na$_2$MoO$_4$ increases, which indicates the increase of the corrosion-resistance of the coatings. The modified phosphate coating was used to automobile castings as an intermediate protect layer before final painting. It was shown that the coating containing molybdate can improve the adhesion of painting onto the automobile casting. Salt spray test and atmospheric corrosion test indicated that the anticorrosion performance of the paint plus phosphate coatings on automobile castings was also improved significantly.

KEY WORDS: phosphate coating; molybdate; salt spray tests.

1. Introduction

Various coating technologies for protecting metal corrosion developed rapidly in recent years. The phosphate coatings are widely applied to metals as underneath layer of paint in mass automobile production. In order to obtain high quality phosphate coating, recent research focuses on the improvement of quality of the phosphate coating by adding some ions, such as Mn$^{2+}$, Ca$^{2+}$, Ni$^{2+}$. Because the crystal size of the casting’s microstructure is larger than that of steel, the phosphate coating on cast iron is usually coarse so the corrosion resistance of the common phosphate coating on casting is limited and cannot sometimes satisfy requirements. There were some investigations on the minimization of phosphate crystal size.

The purpose of this present paper is to present a modified phosphating technique by adding molybdate in the phosphating bath, in order to form the phosphate coating with fine microstructure on the cast iron substrates. The X-ray diffraction and scanning electron microscopy (SEM) were used to investigate the microstructures and compositions of the phosphate coatings, and the phosphating mechanism was discussed. The anticorrosion of the phosphate coating and phosphate plus paint coatings on iron castings were studied.

2. Experiment

Plate specimens of cast iron (No. 30, ASTM) and automobile casting specimens were used for test. The automobile castings included cylinder casting, water pump body, air pump crankcase, cylinder body of clutch pump, cylinder body of air pump. All the specimens were degreased and then submitted to an acid pickling to remove all surface oxides. Then the cleaned specimens were treated in the phosphating bath. The composition of the bath was shown in Table 1. Different concentration of sodium molybdate (0.0–2.0 g/L) were added to the bath to improve the coating quality. The specimens were treatment 7–10 min. The phosphating temperature is 50–60°C. Some of the specimens were painted by alkyd-amine and drying at 180°C.

Phosphate coating weight was measured on the phosphated cast iron samples (50×50×3 mm). Then phosphate coatings on the samples were eliminated in the alkaline bath (100 g/L sodium hydroxide, 90 g/L sodium ethylene diamine tetracetate, 4 g/L triethanolamine, 65–75°C, 15 min). As soon as the coatings were eliminated completely, the samples were dried and weighed. The phosphating coating weight can be calculated according to the equation $W=(W_1-W_2)/S$, where $W$ is the phosphate coating weight,

<table>
<thead>
<tr>
<th>Composition</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85% Phosphoric acid</td>
<td>16-18</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>1.8-2.5</td>
</tr>
<tr>
<td>Zinc nitrate</td>
<td>9.6-12.5</td>
</tr>
<tr>
<td>Manganese nitrate</td>
<td>37.9-40.0</td>
</tr>
<tr>
<td>boric acid</td>
<td>8.3-9.6</td>
</tr>
<tr>
<td>organic amine</td>
<td>1.4-2.7</td>
</tr>
<tr>
<td>citric acid</td>
<td>5.1-6.9</td>
</tr>
<tr>
<td>Sodium molybdate</td>
<td>0, 1.0, 1.5, 2.0</td>
</tr>
</tbody>
</table>
$W_1$ is the sample weight after phosphating, $W_2$ is the sample weight after the phosphate coating was eliminated and $S$ is the surface area of the sample.

The surface observation of the phosphate coating was realized with SEM (JSM-5310, Japan Electronics). The phases in the phosphate coatings were analyzed by XRD (D/max-2500PC, CuKα).

The potential measurement of the phosphate-coated specimens in different phosphating time was conducted in the process of forming of phosphate coatings in phosphating baths containing 0.0 g/L and 2.0 g/L Na$_2$MoO$_4$, respectively. The iron cast samples with the specimen size of 10 mm x 10 mm were used as working electrodes. A saturated calomel electrode (SCE) was used as a reference electrode. Potentials were recorded when the working electrode was immersed from the beginning to 600 s.

The polarization measurement of the phosphate coating specimens was conducted in a 5% NaCl solution. All polarizations were carried out using a SF M273 potentiostat of EG&G. The current was recorded as the potential increased at a scan rate of 50 mV/min.

The adhesion tests of the paint plates (50 mm x 100 mm x 5 mm) were conducted according to ISO 2409 code. Salt spray tests of the paint coating plates (70 mm x 150 mm x 5 mm) and automobile castings were conducted in SF850 salt spray cabinet (Atlas Electric Devices Company). ASTM B117-02 Standard was adopted in the tests. Before salt spray tests two crossed beelines on the surface of samples were scored using the knife (ISO 2409 code). The anticorrosion performance was determined by the breadth of the enlarged rusty along one side of the nick after spray test.

The atmospheric exposure tests of the paint plus phosphate coatings samples (automobile castings) were placed at Changchun (latitude of 44°) in China. Tests were according to the ISO4542 code. The corrosion degree of the samples was evaluated by rust of the coatings exposed to atmosphere circumstance with duration of 3 years.

3. Results and Discussion

3.1. Microstructures of Phosphate Coatings

The iron cast samples were treated according above-mentioned process. The average weight of the phosphate coatings from the phosphating bath contains 0 g/L, 1.0 g/L, 1.5 g/L and 2.0 g/L Na$_2$MoO$_4$, respectively.

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phosphatization treatment and were proved by the XRD results, the possible reactions during the phosphatization of the phosphate coating are:

\[
Fe + 2H_2PO_4^- \rightarrow Fe(H_2PO_4)_2 + H_2 \quad \text{(1)}
\]

The reduction in Eq. (1) resulted in the increase of the local pH at the metal-solution interface, which facilitated the precipitation of insoluble phosphate. Therefore, the reactions forming the insoluble phosphate film occurred:

\[
2\text{Mn}^{2+} + \text{Zn}^{2+} + 2\text{H}_2\text{PO}_4^- + 4\text{H}_2\text{O} \\
\rightarrow \text{Mn}_2\text{Zn(PO}_4)_2 + 4\text{H}_2\text{O} + 4\text{H}^+ \quad \text{(2)}
\]

\[
3\text{Zn}^{2+} + 2\text{H}_2\text{PO}_4^- + 4\text{H}_2\text{O} \rightarrow \text{Zn}_3\text{(PO}_4)_2 + 4\text{H}_2\text{O} + 4\text{H}^+ \quad \text{(3)}
\]

\[
2\text{Zn}^{2+} + \text{Fe}^{2+} + 2\text{H}_2\text{PO}_4^- + 4\text{H}_2\text{O} \\
\rightarrow \text{Zn}_2\text{Fe(PO}_4)_2 + 4\text{H}_2\text{O} + 4\text{H}^+ \quad \text{(4)}
\]

\[
\text{Fe}^{2+} + \text{MoO}_4^{2-} \rightarrow \text{FeMoO}_4 \quad \text{(5)}
\]

Equations (2), (3) and (4) occurred in the traditional phosphatization treatment and were proved by the XRD result. The XRD result of Fig. 2 indicated that one more different substance formed in the phosphate coating with addition of molybdate, that is FeMoO₄. Therefore, the main difference between the microstructures of the traditional phosphate and the present molybdate modified phosphate is the presence of FeMoO₄, an iron molybdenum oxide. The formation of FeMoO₄ may play a role of nucleation for phosphatization. It can be considered that (see Figs. 2, upper diffraction peaks). According to the XRD results, the possible reactions during the phosphatization of the phosphate coating are:

\[
\text{FeMoO}_4 \quad \text{passivation film at the beginning of phosphatization, which should be corresponding to the formation of FeMoO}_4 \text{ passivation film at the beginning of phosphatizing process. Afterwards, the decrease of the potential to more negative signified the dissolution of iron ions into the bath. After phosphating about 50 s, the increase again of the potential represented the formation of phosphate conversion film. The existence of FeMoO}_4 \text{ had been proved by the above XRD analysis.}
\]

It is interesting to note that in the bath with addition of molybdate, the potential tends to be stable after the sample was phosphatized about 370 s, while the potential of the specimen in the molybdate-free bath has no tendency to stop increasing to positive until 600 s phosphating. And the former exhibits a more positive potential than the latter. Therefore, it can be deduced that the addition of molybdate in the bath accelerate the phosphating process.

3.3. Polarization Curves of Black Phosphate Coatings

Figure 4 shows the polarization curves for the coatings obtained from the bath with different concentration of Na₂MoO₄ conducted in a 5% NaCl solution. It is obvious that the corrosion potentials of phosphate coating containing different concentration of Na₂MoO₄ shift to a positive potential with a larger slope than that of molybdate-free coating does. The corrosion potentials (Eₘₚₚ) of the coating from phosphating baths containing 2.0 g/L Na₂MoO₄ shifts positively 167 mV compared with that of the molybdate-free coating. The corrosion current density (iₘₚₚ) decreased from about 1.861 to 0.417 mA/cm². Higher corrosion resistance and lower corrosion current density than the molybdate-free phosphate coating does. The phosphate coatings containing 0.0 g/L and 2.0 g/L Na₂MoO₄, respectively. The potential curve of the iron casting samples in molybdate-free phosphating bath has two distinctive stages. At first stage from 0 to about 100 s, the potential shifted to negative, which implied that the dissolution of iron ions of specimen into the molybdate-free phosphating bath was dominant. After 100 s phosphatation, the potential increased steadily to positive direction. That is, the passivation film formed gradually on the surface of specimen. For the case of phosphatation of iron specimen in the phosphating baths containing 2.0 g/L Na₂MoO₄, there was a rapid shift of potential to positive direction at the beginning of phosphatization, which should be corresponding to the formation of FeMoO₄ passivation film at the beginning of phosphating process. Afterwards, the decrease of the potential to more negative signified the dissolution of iron ions into the bath. After phosphating about 50 s, the increase again of the potential represented the formation of phosphate conversion film. The existence of FeMoO₄ had been proved by the above XRD analysis.

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(from baths containing 1.5 g/L and 2.0 g/L) observed the lowest corrosion current. Hence they can provide better corrosion protection.

3.4. Adhesion Characteristic Tests of the Paint Coating with Phosphate Coating

The paint coatings were coated on the phosphatized iron cast samples, the phosphate coating was employed to intermediate layer obtained from the phosphating bath with different concentration of molybdate. The results of adhesion tests of the paint samples were showed in Table 2. The adhesion test was valuated according the ISO2409 code. That is, a ten-level standard was used to estimate the adhesion quality of paint coating, level 10 indicates the best adhesion and level 1 the worst. It is seen from Table 2 that the underneath phosphate layer do have evident influence on the adhesion characteristics and the phosphate coatings obtained from the bath with addition of 1.5–2.0 g/L Na$_2$MoO$_4$ provided the best adhesion of paint coating to the substrate.

3.5. Result of Salt Spray Tests of the Paint Plus Phosphate Coatings

The results of salt spray test with duration of 1 000 h were shown in Fig 5. The corrosion resistance was evaluated by the enlarged corrosion width of the crossed lines scored previously on the paint surface. It is seen that the paint coated on molybdate-free phosphate coating samples possess relatively lower corrosion resistance, shown by a wider corrosion width (Fig. 5(a)). The increase of the concentration of molybdate in the phosphating bath resulted in an evident increase of the corrosion resistance of the paint plus phosphate coatings, shown by the decreasing enlarged corrosion width.

3.6. Atmospheric Corrosion Tests of Automobile Castings

The atmospheric corrosion test is a simple but effective method for estimating the corrosion property of the samples in real situations, although it is time-consuming. Because the proposed modified phosphate coatings will be applied to protect the automotive components, several iron casting parts including water pump body, air pump crankcase, cylinder body of clutch pump, cylinder body of air pump were phosphated with the present bath and then painted. Afterward, 3 samples of every casting part were put outdoor under an umbrella-shape roof in order to simulating the practical condition. Table 3 shows the results of the atmospheric corrosion tests with duration of 3 years of these automobile castings. It is seen that the iron castings protected with the present modified phosphate coatings (obtained from the bath containing 1.5–2.0 g/L Na$_2$MoO$_4$) plus paint can sustains 3 years without rust corrosion, while the contrastive ones treated with the traditional phosphatization were all eroded in atmosphere.

4. Conclusions

(1) The microstructure in the phosphate coatings on cast iron surface can be greatly modified by addition of sodium molybdate to the phosphating bath. Fine and equa-axis grains of phosphate were obtained with the addition of 1.5–2.0 g/L sodium molybdate in the phosphating bath.

![Fig. 4. Polarization curves of phosphate coatings on cast iron, from phosphate bath containing different concentration of Na$_2$MoO$_4$.](image)

![Fig. 5. Salt spray test of paint plus phosphate coatings on cast iron, with the phosphate coatings obtained from the baths containing different concentration of Na$_2$MoO$_4$: (a) 0.0 g/L, (b) 1.0 g/L, (c) 1.5 g/L and (d) 2.0 g/L.](image)
(2) The molybdate modified phosphate coatings possess good corrosion resistance and excellent adhesion property to paint compared with the common phosphate coating without molybdate.

(3) The molybdate modified phosphate plus paint coatings on cast iron exhibits excellent corrosion resistance in both salt spray and atmospheric circumstance.

Acknowledgments

The authors gratefully acknowledge the Foundation of national key basic research and development program No.2004CB619301 for the provided support of this work.

<table>
<thead>
<tr>
<th>Parts</th>
<th>Na$_2$MoO$_4$ concentration in the phosphating bath (g/L)</th>
<th>0</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylinder casting</td>
<td>32.7% rust area</td>
<td>23.1% rust area</td>
<td>rustless</td>
<td>rustless</td>
<td></td>
</tr>
<tr>
<td>Water pump</td>
<td>20.6% rust area</td>
<td>rustless</td>
<td>rustless</td>
<td>rustless</td>
<td></td>
</tr>
<tr>
<td>Air pump</td>
<td>57.2% rust area</td>
<td>28.4% rust area</td>
<td>rustless</td>
<td>rustless</td>
<td></td>
</tr>
<tr>
<td>Cylinder body</td>
<td>16.3% rust area</td>
<td>rustless</td>
<td>rustless</td>
<td>rustless</td>
<td></td>
</tr>
<tr>
<td>Cylinder body</td>
<td>7.2% rust area</td>
<td>rustless</td>
<td>rustless</td>
<td>rustless</td>
<td></td>
</tr>
</tbody>
</table>

REFERENCES