Effects of nano-MoS$_2$ additive on manganese phosphate composite conversion coating of carbon steel

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Manganese phosphate is an industrial coating material used to reduce friction and improve lubrication in sliding components. In this study, the morphology and tribological properties of uncoated carbon steel and carbon steel coated with only manganese phosphate and with manganese phosphate with nano-MoS$_2$ were investigated. This work shows the effects of nano-MoS$_2$ on the formation of manganese phosphate coatings on steel. The manganese phosphate composite conversion coatings are created by chemical treatment, and the main component of the layer is hureaulite $(\text{Mn,Fe})_5\text{H}_2(\text{PO}_4)_4\cdot4\text{H}_2\text{O}$. With regard to the effects of nano-MoS$_2$ on the surface of composite coatings, it is obvious that the crystals of coatings formed more compactly with an increase in the nano-MoS$_2$ content from 0 to 5 g/L. The surface microstructure of the coatings formed in a bath with nano-MoS$_2$ was more uniform than that formed in a bath without nano-MoS$_2$. It can be seen that there is a decrease in the size of the domed structure and in the surface roughness as the content of MoS$_2$ increased in the nanocomposite coatings. The effect of MoS$_2$ on the friction and wear behaviors of composite conversion coatings at 3 g can be a very effective deterrent for tribological of decrease.

Key words: Manganese phosphate coating, Nano-MoS$_2$, Carbon steel, Morphology, Composite chemical treatment.

Introduction

The phosphating of steel, galvanized steel, zinc, and sometimes aluminum represents an essential chemical conversion method for metal surface finishing in many industries such as automotive components and domestic appliances [1-3]. Phosphating is a surface treatment process for preparing a surface prior to the deposition of a protective layer on metallic surfaces. Phosphate coatings are generally formed by immersing steel into an aqueous solution of phosphoric acid and manganese carbonate. Manganese phosphate coating has the highest and superior corrosion and wear resistances of general phosphate coatings.

Manganese phosphating is extensively employed to improve the sliding properties of engines, gears, and power transmission systems. The use of manganese phosphate coatings for improved corrosion resistance can be found in virtually all branches of the metalworking industry. Typical examples include motor vehicle components in brake and clutch assemblies, engine components, leaf or coil springs, casting interiors, and many other small items. Manganese phosphate conversion coatings confer good corrosion resistance, whether a post-treatment such as an oil application is used, and are invariably applied by the immersion method. Phosphate coatings are commonly employed to improve the corrosion and wear resistance of ferrous and nonferrous metals. Phosphate coating combines divalent metal (Me) ions with phosphate multihydrate ($(\text{PO}_4)_2\cdot\text{xH}_2\text{O}$) to form an insoluble film on a metal surface.

Composite coating technology is an efficient way of surface finishing and engineering. Composite coatings can be prepared by suspending micro- and nanosized particles on metal, nonmetal, and even polymer. Coatings containing solid particles of carbides, carbon tubes, oxides, sulphides, and diamonds have been developed for better wear resistance, corrosion resistance, and dispersion hardening [4-9]. In particular, the protective properties of these coatings are strongly correlated to both the type and dimension of the second phase [10], its distribution, and the incorporation content and layer microstructure [11, 12]. Layered materials such as molybdenum disulphide (MoS$_2$) or tungsten disulphide (WS$_2$) are widely used as solid lubricants or as additives in liquid lubricants [13].

Transition metal dichalcogenides such as molybdenum disulphide and tungsten disulphide possess unique anisotropic crystal structures. Metal and chalcogen elements are combined with strong covalent bonding in the plane, and there is merely a weak Van der Waals force between the adjacent lattice layers. Thus, a slip between crystal lamellar sheets easily occurs. Therefore, transition metal dichalcogenides, especially for MoS$_2$, are widely used.
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as solid lubricating films and lubricating oil additives [14]. For better tribological performance, this is an effective way to combine the advantages of liquid lubricants as a novel lubrication technology. Z. Hui [15] reported that pure MoS$_2$ coating exhibits poor tribological behavior because the wear rate is higher although its friction coefficient is much lower, whereas MoS$_2$-Ti composite coatings have low friction coefficients and low wear rates. From the above literature, it is revealed that manganese phosphate coating is included in the family of wear resistance coatings. This study evaluates the effects of nano-MoS$_2$ as an additive in manganese phosphating baths for carbon steel.

**Experimental**

**Preparation of Mn-P-MoS$_2$ coatings**

The substrate used for the phosphating treatment was an SM45C alloy steel with a chemical composition (wt.%) of 0.46 C, 0.17 Si, 0.73 Mn, 0.018 P, 0.01 S, and balanced Fe. Samples with dimensions of 25 mm × 25 mm × 1 mm were polished with SiC papers of successively finer grit down to 2000. The polished samples were degreased by acetone in an ultrasonic bath for 5 min and rinsed in distilled water. The optimal contents of the chemical compositions of manganese phosphating recipes and operating conditions are listed in Fig. 1. The phosphating treatments were carried out at about 95 °C for 5 min. The molybdenum disulfide (square-shaped) nanoparticles were characterized by high-resolution transmission electron microscopy (HRTEM), as shown in Fig. 2. The results showed that the size of the as-prepared molybdenum disulfide nanoparticles with layered structures was in the range of 80-100 nm. In order to create a more stable suspension of the ceramic powders, the composite chemical treatment baths were treated by ultrasound for 30 min and mechanically stirred for 24 h before use. Many works have reported a beneficial effect of ultrasound in refining the grain size of the composite coatings [15-20].

**Characterization of Mn-P-MoS$_2$ coatings**

After the phosphate-permanganate conversion coating process, samples were sectioned perpendicularly to the metal interfaces and then mounted on epoxy resin. The surface and cross-section morphologies of the conversion coating layers were observed using a scanning electron microscope (SEM, Hitachi S-4300, Tokyo, Japan) coupled with energy dispersive X-ray spectrometry (EDS). The surface topography and heterogeneities of Mn-P and Mn-P-MoS$_2$ were examined by atomic force microscopy (AFM). Measurements were performed under ambient conditions using standard topography AC air (tapping mode in air). An AFM head scanner was applied with a Si cantilever vertically adjacent, with the sample resonant frequency of the free oscillating cantilever set as the driving frequency.

X-ray diffraction (XRD) was performed with a goniometer to identify the crystal structures of conversion coating layers under measurement conditions (40 kV, 35 mA) of Cu-K$_\alpha$ for the X-ray source. The specimens were run to at 20 from 5 ° to 60 ° with a step size of 0.01° (2θ) and a scanning rate of 4 °/min. The chemical states of some typical elements on worn surfaces were determined using a PHI-5702 X-ray photoelectron spectroscope (XPS) at a pass energy of 29.4 eV and a resolution of ± 0.2 eV, using Al K$_\alpha$ radiation as the excitation source and the binding energy of adventitious carbon (C 1s: 284.8 eV) as the reference.

The tribological properties of the coatings were tested by ball-on-disc friction and a wear tester at a humidity between 30 and 50% in air. The tests were performed at 5 N at diameters of 24 mm. The sliding speed was 1,257 m s$^{-1}$ (1000 rpm). An 8-mm-diameter
440C stainless steel ball was used as the counterpart. The corrosion resistance of the coating layers was configured in 3.5% NaCl solution using potentiodynamic polarization and electrochemical impedance techniques. Tests were carried out in a three-electrode cell (where the working electrode was the coating layer) using a Bio-Logic potentiostat/galvanostat equipped with the software EC-Lab version 10.2. A potentiodynamic scan was carried out in the range of -250 mV to +250 mV vs. the open-circuit potential using a scan rate of 1 mV s⁻¹ at a constant temperature of 25 °C.

Results and Discussion

Weight of Mn-P-MoS₂ coating

The results of the conditions of the Mn-P bath with nano-MoS₂ are listed in Table 1. The acidity of the bath [free acid (FA) and total acidity (TA)] as well as the ratio between them must be maintained at an optimum level to obtain a uniform coating of good thickness. Fig. 3 shows the variations of the TA/FA with a manganese phosphate bath containing different contents of nano-MoS₂. The conversion of soluble primary phosphates into insoluble tertiary phosphates occurs with the regeneration of phosphoric acid. Therefore, stable manganese phosphate baths require a certain amount of free phosphoric acid to suppress hydrolysis and to maintain an effective deposition rate. However, the presence of excess phosphoric acid may retard the formation of the coating and lead to an excessive loss of metal.

The weight of the phosphate coatings obtained after the surface is treated in phosphating baths containing different contents of nano-MoS₂ is shown in Fig. 4. It is clearly seen that the phosphate coatings formed in the bath with nano-MoS₂ until 3 g/L are heavier than those formed in the bath without nano-MoS₂. This is because the faster phosphating reaction was caused by nano-MoS₂. The weight of the phosphate coatings increased approximately linearly with the nano-MoS₂ content in the bath from 0 to 3 g/L. These analyses confirmed that the existence of nano-MoS₂ influenced the formation of the phosphate coating. On the other hand, a 5-g/L decrease inhibited the growth of Mn-P coatings.

### Table 1. Ratio of TA/FA in Mn-P-MoS₂ composite chemical treatment.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Total acid (TA)</th>
<th>Free acid (FA)</th>
<th>Acid ratio (TA/FA)</th>
<th>pH</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-P solution (Non-additive)</td>
<td>100</td>
<td>19</td>
<td>5.3</td>
<td>2.05</td>
<td>2.05</td>
</tr>
<tr>
<td>Mn-P solution (+ 1g MoS₂)</td>
<td>92</td>
<td>18</td>
<td>5.1</td>
<td>2.08</td>
<td>97</td>
</tr>
<tr>
<td>Mn-P solution (+ 3g MoS₂)</td>
<td>90</td>
<td>18</td>
<td>5.0</td>
<td>2.08</td>
<td>2.08</td>
</tr>
<tr>
<td>Mn-P Coating (+ 5g MoS₂)</td>
<td>82</td>
<td>17</td>
<td>4.8</td>
<td>2.06</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Morphology and microstructure

The effects of MoS₂ nanoparticles on the surfaces of composite coatings are illustrated in Fig. 4. As can be seen, the addition of MoS₂ nanoparticles brings about the homogeneous dispersion of nanoparticles in the Mn-P matrix. It can be seen that the surface morphology of Mn-P was greatly affected by the amount of MoS₂ used. It is obvious that the crystals of the coatings formed more compactly with an increase in nano-MoS₂ content from 1 to 5 g/L. By comparison, the surface microstructures of the coatings formed in the bath with nano-MoS₂ were more uniform than those formed in the bath without nano-MoS₂. The phosphate coating obtained in the bath containing 3 g/L of nano-MoS₂ was the most compact and had a more general size of crystal. The morphology of Mn-P-MoS₂ resulted in composite nanocrystalline grains.

The results of an EDX analysis of the MoS₂ nanocomposite coating are shown in Fig. 5, which presents variations in the atomic percentages of Mn, P, Mo, and S in the nanocomposite coating with a varying amount of MoS₂ in the manganese phosphate bath. The increase in MoS₂ concentration in the manganese phosphate bath led to an increase in Mn, P concentration. It is shown that the nano-MoS₂ had a significant effect on the density and size of the crystals. AFM micrographs of Mn-P and Mn-P-MoS₂ nanocomposite coatings are shown in Fig. 6. It can be seen that there is an increase in the size of the domed structure and surface roughness with an increasing content of MoS₂ in the nanocomposite coatings. The surface roughness was expressed by an average deviation parameter (Ra). This value gives the average height of irregularities in a direction perpendicular to the surface. The flat and smooth profiles of the MoS₂ molecules cause low friction.

Mn-P-MoS₂ coating structure

XRD patterns of phosphate coatings obtained from baths containing different contents of nano-MoS₂ are
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It is evident that manganese iron hydrogen phosphate hydrate, referred to as iron hureaulite [(Mn,Fe)$_5$H$_2$(PO$_4$)$_4$·4H$_2$O]; manganese phosphate hydroxide hydrate, referred to as manganese hureaulite [Mn$_5$(PO$_4$)(OH)$_2$·(PO$_3$H)(H$_2$O)$_6$]; and manganese hydrogen phosphate hydrate [MnHPO$_4$·2.25H$_2$O] are the predominant phases. In addition, the diffraction pattern of this coating also exhibits peaks pertaining to MoS$_2$. The presence of MoS$_2$ peaks confirms it is a composite with other manganese phosphates in the coating. A comparison of the XRD patterns of Mn-P-MoS$_2$ composite conversion coatings reveals that they have similar phase contents.

Fig. 8 shows an XPS analysis of Mn-P-MoS$_2$ composite conversion coating that indicates the presence of Mn, P, Mo, and S. The high-resolution spectrum of Mn 2p indicates two distinct peaks: Mn 2p$_{3/2}$ at 641.7 eV and Mn 2p$_{1/2}$ at 653.7 eV, with respective area ratios of 1.41/2 and 0.59/2, which can be assigned to Mn$^{2+}$. The peak pertaining to the oxygen of metal oxide that commonly appears at 530 eV could not be identified, which suggests the absence of any metal oxides in the coating. The asymmetric P 2p peak can be deconvoluted into two peaks at 131.8 eV and 133.6 eV. The peaks at 133.6 eV and 131.8 eV, with area ratios of 1.23/2 and 0.77/2, can be ascribed to (HPO$_4$)$_2$ and (PO$_4$)$_3$, respectively.

The XPS spectra of the Mo 3d region for molybdenum has peaks at 229 and 232.4 eV, which are characteristic of MoS$_2$ and can be attributed to 3d$_{5/2}$ and 3d$_{3/2}$, respectively. The spectra were then fitted into two doublets arising from Mo$^{5+}$ 3d$_{5/2}$/Mo$^{5+}$ 3d$_{3/2}$ and Mo$^{4+}$ 3d$_{5/2}$/Mo$^{4+}$ 3d$_{3/2}$ signals. The spectrum is fitted at 162.5 eV. This is attributed to a sulfide species. S 2p$_{3/2}$ binding energy values for MoS$_2$ were reported in the
range of 161.6 to 162.4 eV. There appears to be a small contribution near 160.8 eV. This contribution is not always present, however, and may result from the presence of a highly reactive surface state.

**Effect of MoS$_2$ contents of friction**

Table 2 lists the values of the average friction coefficients and roughness for Mn-P-MoS$_2$ composite coatings. It can be seen that the average friction coefficient of Mn-P-MoS$_2$ composite coating decreases from 1 g to 5 g of nano-MoS$_2$ additive.

The characteristics of uncoated carbon steel and carbon steel coated with only manganese phosphate and with manganese phosphate with nano-MoS$_2$ were examined using a ball-on-disk apparatus, and the results are shown in Fig. 9. The MoS$_2$ lubrication effect improves by decreasing the surface roughness owing to the addition.

The wear loss of manganese phosphate coated with MoS$_2$ is lower than that with only a manganese phosphate coating because a significantly lower coefficient of
friction was exhibited. It is obvious that the incorporation of MoS₂ nanoparticles in the Mn-P matrix, owing to the self-lubricating properties of these particles, leads to a significant reduction in the friction coefficient of the coating.

Conclusions

The weight of phosphate coatings increased approximately linearly with increasing nano-MoS₂ content in a bath from 0 to 5 g/L. Results of analyses confirmed that the existence of nano-MoS₂ influenced the formation of the phosphate coating. The morphology and structures of Mn-P-MoS₂ composite conversion coatings are affected by the incorporation of nano-MoS₂ particles into the manganese phosphate bath. The friction coefficient of manganese phosphate coated with 3 g of MoS₂ is lower than that for only-manganese-phosphate-coated pins because of a significantly lower coefficient of friction that was exhibited. It is obvious that the incorporation of MoS₂ nanoparticles in the Mn-P matrix, owing to the self-lubricating properties of these particles, leads to a significant reduction in the friction coefficient of the coating. Manganese phosphate with MoS₂ coating shows a very low coefficient of friction compared with manganese phosphate coating. The average coefficient of friction is around 0.0378 under 5-N loads with a sliding velocity of 1.257 m/s. The reason is that the MoS₂ lubricant has improved its properties in terms of both friction and particle refinement.

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References