Abstract

Due to containing some alloy elements such as chromium, 30CrMnMoTi steel is usually difficult to be phosphated. In present paper, the growth process of the phosphate coating on 30CrMnMoTi alloy steel fabricated by a high temperature manganese phosphating was investigated. The microstructure, surface morphology, composition and corrosion resistance of the phosphate coatings were analyzed by XRD, SEM, EDS and electrochemical polarization method, respectively. The time dependence of open circuit potential (OCP) and the weight of the coating were also measured. It is found that the phosphate coating is mainly composed of \((\text{Mn,Fe})_5\text{H}_2\text{(PO}_4\text{)}_4\cdot4\text{H}_2\text{O}\) and consists of a lot of close packed lump crystallites. Based on the time dependence of morphology and the weight of phosphate films, it shows that the phosphating process mainly includes three stages: corrosion of the substrate, creation and growth of phosphate crystal nucleus and thickening of phosphate coating. For 30CrMnMoTi steel, it takes at least 30 seconds and 3 minutes for the first and second step, respectively: at the beginning stage of phosphating process, a lot of bubbles emit, then a complete film will form at the end of bubbling, and the nucleation of phosphate film is inhomogeneous, phosphate crystal nucleus usually forms preferentially at grain boundary. The coating weight—time curve is similar to that of the parabolic growth. The electrochemical polarization measurement shows that the corrosion potentials of the phosphated steel shifted positively about 480 mV than the bare steel and the results of neutral salt spray test (NSS) could reach 24h, indicating the phosphating improved the corrosion resistance of the 30CrMnMoTi alloy steel.

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Keywords: manganese phosphate coating; 30CrMnMoTi alloy steel; corrosion resistance; phosphating mechanism.

1. Introduction

As a material with good mechanical properties, 30CrMnMoTi alloy steel is widely used in many industrial fields. But its poor resistance to corrosion has seriously affected its application. In order to improve the corrosion prevention and wear resistance, one way is to form a dense, finely-structured and firmly phosphate coating on the
steel [1–3]. Due to manganese phosphate coating has the highest hardness and superior corrosion and wear resistances among the three most common used phosphate (zinc, iron and manganese) [4-6], for decades, it has been specified as a good choice for a large percentage of steel and iron ordnance components which need excellent corrosion resistance [7-10]. To get a good manganese phosphating coating, a more effective and environmentally-friendly way is still underway to research [11–14]. Yasar Totik studied the influences of different substrate heat treatments on corrosion property of phosphate coatings formed on AISI 4140 steel [15]. Chao-Min Wang et al. investigated the effects of temperature and applied potential on the microstructure and electrochemical behavior of manganese phosphate coating on CrMoV steel [16]. Owing to different phosphating behavior and corrosion property will occur on the different substrate steel, thus in this study, the growth process and the corrosion resistance of manganese phosphate coating formed on 30CrMnMoTi alloy steel were investigated, then the phosphating mechanism was discussed.

2. Experimental

30CrMnMoTi alloy steel samples with the specimen size of 50×10×5 mm were used as the substrates. The compositions of the alloy are given in Table 1. The samples were grinded using No. 1500 sand papers. The treatment implemented for the study is described in Table 2. The manganese phosphatation mainly consists of four sequences: degreasing, pickling, activating, actual phosphating. After degreasing (50g/L non-phosphor degreaser solution) and rinsing, a pickling sequence is implemented to remove all surface oxide and dirt. Then after rinsing, activating was implemented, or else the high temperature phosphating bath would lead to a quite thick coating with coarse crystallization. The activating bath, consisting of Mn-phosphate and Na-carbonate solution, favors the deposit of a fine layout of metallic salts on to the steel surface. These germination sites allow the building up of fine phosphate crystals and therefore the coating is dense and homogeneous. Then the substrates were coated in a phosphate coating bath at a temperature of 95-100°C. The phosphating bath containing Mn(H₂PO₄)₂, Ni(NO₃)₂, tartaric acid and concentrated solution of ferrous phosphate which is a ferrous ion concentrated solution by the reaction of a certain amount iron powder and a certain concentration of phosphoric acid. Tartaric acid is an agent to complex with iron ions in the solution to reduce sedimentation. The total acid and ferrous iron content in concentrated solution of ferrous phosphate are 650 and 47.47g/L. Ni(NO₃)₂ and tartaric acid in the phosphating bath are 4g/L and 2g/L respectively. The conditions of phosphate coatings are as follows: total acid: 100 point, free acid: 18point, iron content: 1.0g/L, activate time: 20s, phosphating time: 0~15min.

Table 1 The compositions of 30CrMnMoTi alloy steel (in wt.%)

|   | Mo | Ti | Ni | Cr | Cu | S | P | Mn | Si | C | Fe |
|---|----|----|----|----|----|---|---|----|----|---|----|
|   | 0.270 | 0.077 | 0.058 | 1.160 | 0.060 | 0.021 | 0.020 | 0.770 | 0.326 | 0.328 | Balance |

Table 2 Manganese phosphatation treatment

| Treatment          | Condition                           |
|--------------------|-------------------------------------|
| Degreasing         | 50g/L non-phosphor degreaser solution, 70~80°C, 15min |
| Rinsing            | Water, 60~70°C                       |
| Rinsing            | Water, room temperature              |
| Pickling           | 50g/L H₃PO₄ solution, room temperature, 20s |
| Rinsing            | Water, room temperature              |
| Activating         | 1.5g/L Mn₃(PO₄)₂ and 1.5g/L Na₂CO₃ solution, 60~70°C, 20s |
| Phosphating        | Manganese phosphating solution, 95~100°C |
| Rinsing            | Water, 60~70°C                       |
| Rinsing            | Water, room temperature              |
| Drying             | Warm air steam                       |

The morphology and compositions and the phases of the formed coating were analyzed by SEM(TESCAN VEGAI, Czech), EDS and XRD, respectively. In order to observe the growth of the phosphate coating, the phosphating time dependence of coating weight and open circuit potential (OCP) were measured. The amount of manganese phosphate coating(W) on the surface of 30CrMnMoTi alloy steel was obtained by measuring the final weight of the coated specimen(W₂) and the weight after removing the coating(W₁), respectively, then W=W₂-W₁. The weight was measured to an accuracy of ±0.1 mg. In order to obtain a reliable and accurate value of W₁, the coated specimen was cleaned in 5 wt.% CrO₃ solution at 75 °C for 15 min in accordance with MIL specification [17]. The OCP was measured from the beginning of phosphating to about 15min by immersing the working electrode in the phosphating bath, while a saturated calomel electrode (SCE) was used as a reference electrode.
The corrosion resistance of the phosphate coating was analyzed with a LK98B electrochemical analysis instrument by using a three-electrode cell: SCE for the reference electrode, a platinum electrode for the counter electrode, and the coated sample (area: 1 cm×1 cm) used for the working electrode. The electrochemical polarization measurements were conducted in 3.5 wt.% NaCl solution at 25 °C.

3. Results and Discussion

3.1 The growth of the phosphating coating

![SEM images of the manganese phosphate coating on the 30CrMnMoTi alloy steel at different phosphating time](image)

Fig. 1. SEM images of the manganese phosphate coating on the 30CrMnMoTi alloy steel at different phosphating time: (a) 30 s, (b) 1 min, (c) 3 min, (d) 5 min, (e) 7 min, (f) 15 min

The surface morphology (×1000) of the phosphate films on the 30CrMnMoTi alloy steel at different phosphating time is shown in Fig. 1. Fig1(a) shows the surface morphology of the sample immersed in the bath for 30 s. During this period, a lot of bubble emitted from the metal surface. Many small crystal grains formed non-uniformly on the surface, which have an average size of 3–4 μm, mainly distributed at grain boundaries. In order to prove this, the metallographic images on the bare substrate and phosphated surface were conducted. Fig 2(a) and (b) are the metallographic images (×2000) of the bare 30CrMnMoTi alloy steel and phosphate film of 30 s after immersion in the phosphating bath respectively. By comparing Fig2(b) with Fig2(a), it is found that the crystal nucleus formed non-uniformly at the grain boundaries of the surface. It is also seen that other sites of the substrate were etched like honeycomb. It is indicated that the grain boundaries are the micro cathode sites and the phosphate crystal nucleus forms preferentially at grain boundary.
Fig1(b) shows the growth process of phosphating film at the time of 1min. At this time, there were still a lot of bubbles emitted from metal-solution interface. The particles grew quickly to form bigger particles of about sizes of $6-7\mu m$, and some new small crystal particles formed on the bigger ones (Fig.1(b)1). But the substrate was not fully covered by phosphating film (Fig.1 (b)2). This corresponded with bubble emitting.

When it came to 3min (Fig1(c)), the film fully covered the surface and bubble emitting disappeared. A complete film formed on the surface. We called this periods “bubbling time”. Fig1 (d), (e) and (f) shows growth process of phosphating film at different times of 5min, 7min and 15min. In this stage, the crystal particles grew bigger and new crystal nucleus formed on the gaps of grains. Phosphate coating grains packed like leaves and finally formed a dense film. The phosphating film with a dense structure will have a good corrosion resistance.

![Fig.2. Metallographic images of the 30CrMnMoTi alloy steel substrate (a) and 30s after immersion in the phosphating bath(b)](image)

### 3.2 Open circuit potential (OCP)

Fig.3 and Fig.4 shows the variations of coating weight and open circuit potential (OCP) during phosphatization, which represent the growth rate of phosphate film. It can been seen that at the initial stage of phosphating process, the coating weight increased rapidly. As phosphating process went on, the increase of coating weight gradually slowed down. The coating weight-time curve is similar to that of the parabolic growth.

The OCP–time curve obtained for the present study could be analyzed by dividing them in to three segments as follows:

Segment I: change in potential from initial to most negative value
Segment II: change in potential from most negative to most positive value
Segment III: fluctuated in potential in a small range

#### 3.2.1 Segment I

As the substrate immersed in the bath, a lot of bubble emitted at metal-solution interface, the OCP shifts rapidly to a negative position in the initial period, and finally reaches a most negative value (about 30s). This negative shift in potential is due to the depletion of $H^+$ ions at the metal-solution interface caused by the attractive force from electrons released by metal solution. It implied that the metal dissolved rapidly during this stage. Figure 2(b) also confirms that the substrate was etched like honeycomb and some crystal nucleus formed on the surface. Metal dissolution is the predominant reaction during this segment.

#### 3.2.2 Segment II

The OCP shifted rapidly to a positive position and finally reached the most positive value (about 180s). The potential shift observed in this segment is due to the deposition of insoluble phosphate on the substrate. Figure 1(a), (b) and (c) shows that, in this stage, the crystal nucleus formed and grew quickly on the metal surface, finally the substrate surface was covered by phosphate film at about 3min, and the coating weight increase rapidly. Thus, formation and quick growth of crystal nucleus are the main reaction during this segment.

#### 3.2.3 Segment III

It was observed that OCP fluctuated in a small range and the phosphate coating weight tended to grow slowly. Fluctuation in OCP can be attributed to the competitive processes of passivation and film dissolution during the phosphating process[16]. The reactions of dissolution and re-precipitation could take place. These processes could then lead to crystalline re-organization and result in a net decrease in coating porosity and the phosphate coating become dense and there is no gap or crack on the phosphate film.
3.3 XRD of Phosphating film

Fig.5 shows the XRD pattern of the sample immersing in the bath for 15min. It is seen that phosphate coating is composed of (Mn,Fe)$_2$H$_2$(PO$_4$)$_4$·4H$_2$O, MnFe$_2$(PO$_4$)$_2$·H$_2$O and Mn$_9$Fe$_2$(PO$_4$)$_8$·14H$_2$O, and the first one is the main phase.

In the present phosphating process, Mn(H$_2$PO$_4$)$_2$, concentrated solution of ferrous phosphate and Ni(NO$_3$)$_2$ were added in the bath. Mn(H$_2$PO$_4$)$_2$ dissolved in the solution to produce:

$$Mn(H_2PO_4)_2 \leftrightarrow MnPO_4^- + H_2PO_4^- + 2H^+$$ (1)
The complex ion $\text{MnPO}_4^-$ has the ionization reaction as follows:

$$\text{MnPO}_4^- \leftrightarrow \text{Mn}^{2+} + \text{PO}_4^{3-} \quad (2)$$

It is generally recognized that phosphating is an electrochemical process in nature. During phosphatization, as soon as the substrate metal soaked in the phosphate bath, the surface of the substrate divided into micro anode sites and micro cathode sites and the reactions on the surfaces should be thought to take place on different local polarization sites correspondingly. As to 30CrMnMoTi alloy steel, crystal grain boundary of the steel is regarded as the cathode sites[18] and other parts of the metal the anode sites. Therefore, the following reaction can occur at the micro anode sites:

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{(anodic)} \quad (3)$$

At the micro cathode sites hydrogen ions were reduced simultaneously:

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \uparrow \quad \text{(cathodic)} \quad (4)$$

In the phosphating bath, $\text{Ni(NO}_3)_2$ has two actions. First, it provides $\text{Ni}^{2+}$ in the solution which can reduce the coating crystal size:

$$\text{Ni(NO}_3)_2 \rightarrow \text{Ni}^{2+} + 2\text{NO}_3^- \quad (5)$$

Then $\text{NO}_3^-$ can accelerate the deposition of insoluble phosphate:

$$\text{NO}_3^- + 10\text{H}^+ + 8e^- \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O} \quad (6)$$

The dissolution of Fe at local anodic sites causes reduction of either H$^+$ or a coating bath additive $\text{NO}_3^-$ at local cathodic sites. The resulting increase in local pH causes equilibrium (1) and (2) to shift to the right, driving the precipitation of insoluble phosphate:

$$5\text{Mn}^{2+} + 5\text{Fe}^{2+} + 4\text{H}_2\text{PO}_4^- + 4\text{H}_2\text{O} + 6e^- \rightarrow (\text{Mn},\text{Fe})_5\text{H}_2(\text{PO}_4)_4\cdot 4\text{H}_2\text{O} + 3\text{H}_2 \uparrow \quad (7)$$

Here $(\text{Mn,Fe})_5\text{H}_2(\text{PO}_4)_4\cdot 4\text{H}_2\text{O}$ is the main ingredient of the phosphate coating. The XRD pattern of the sample also confirms this.

As mentioned above, metal dissolution can cause reduction of $\text{NO}_3^-$ and H$^+$. The rate of depletion of H$^+$ has an important impact on growth of phosphating film. As showed in Figure 3, because of the quick depletion of H$^+$, phosphating film grew quickly and the coating weight increased rapidly from initial to 3min, and then since the substrate was fully covered by phosphating film and metal dissolution became slow, the coating weight increased slowly.

### 3.4 Corrosion resistance of the phosphate coating

![Fig.6. Polarization curves for the 30CrMnMoTi alloy steel (a) with and (b) without the phosphate coating on it.](image)

The polarization curves of the 30CrMnMoTi alloy steel substrate with and without the phosphate coatings is given in Fig.6. The cathode reaction in the polarization curve corresponded to the evolution of the hydrogen, and the anodic polarization curve was the most important features related to the corrosion resistance of the coatings. Current density increases with increasing anodic over-voltage through the entire range of anodic polarization. The corrosion
potentials (Ecorr) shifted positively about 480 mV from about -980 mV of the bare 30CrMnMoTi alloy steel to about -500 mV of coatings.

Neutral salt spray test (NSS) with Chinese national standards of GB/T 10125-1997 was also carried out. The results of NSS could reach 24h which far exceeded the standard for industrial applications (1.5h). The phosphating process has already applied to industrial production. Therefore, the phosphate coatings exhibit higher corrosion resistance than the 30CrMnMoTi alloy steel substrate, and high corrosion resistance of the phosphate coating will be expected.

4. Conclusions

A manganese phosphate coating was formed on 30CrMnMoTi alloy steel. The phosphate coating consists of lots of close packed lump crystallites and mainly composed of (Mn,Fe)5H2(PO4)4·4H2O. The phosphate coating is formed by three steps: corrosion of the substrate, creation and growth of phosphate crystal nucleus and thickening of phosphate coating; for 30CrMnMoTi steel, it takes at least 30 seconds and 3 minutes for the first and second step respectively. The corrosion potentials of the steel with the phosphate coatings in 3.5 wt.% NaCl solution shifted positively about 480 mV than the bare steel and the results of NSS could reach 24h, means, the phosphating can improve the corrosion resistance of the 30CrMnMoTi alloy steel.

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