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Short Communication

Effect of Manganese Phosphating on Properties of 45 Steel Used for Gear Production

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Phosphating technology was utilized to improve the corrosion resistance and wear resistance of gear, allowing it to last significantly longer. The phosphating film formed on the gear surface was described and examined in terms of appearance, surface morphology, composition, thickness, corrosion resistance, and wear resistance. The results show that the appearance of the gear treated with conventional manganese phosphating or manganese composite phosphating is both black. However, after the treatment of manganese composite phosphating, many PTFE particles doping on the grains and gaps play a physical filling role. The PTFE has self lubrication performance with higher impedance which could block the penetration of corrosive medium and form a layer of solid lubricating film to greatly reduce corrosion and wear. The gear that has been phosphated with manganese composite solution offers the best corrosion resistance and wear resistance.

Keywords: Gear; Manganese composite phosphating; Corrosion resistance; Wear resistance

1. INTRODUCTION

Gear is a mechanical component to continuously transfer motion and power used in industrial fields. Industry is the foundation of a country's national economy, and gear manufacturing is one of the important signs of industrializations. Gear has become the core transmission component in the machinery manufacturing industry due to its advantages of precise transmission, high transmission power and high efficiency. With the development of science and technology, gear is widely used in various fields of modern industrial manufacturing [1-5]. However, gear is prone to wear due to bearing alternating loads in the working environment. In addition, the working environment of gear is special, often contains corrosive medium, so the gear is required to have good corrosion resistance and wear resistance. The common gear is made of copper, steels, aluminum alloys and so on. Therefore, many surface treatment technologies can be used to improve the corrosion resistance and wear resistance, such as plating technology, electroless deposition, anodic oxidation, carbonitriding, shot peening, phosphating and so on [6-13]. Each technology has different principles and is suitable for the gear surface treatment under different working conditions. Among them, the phosphating treatment has the advantages of low cost, simple operation and controllability. It is found that he phosphating film is not conductive with good corrosion resistance. In addition, the porous crystalline structure of the phosphating film can effectively improve the lubrication condition to reduce the friction coefficient which has been reported in many literatures [14-18]. As a result, it can be inferred that phosphating treatment can improve the corrosion resistance and wear resistance of gear. The phosphating coating on the surface efficiently prevents corrosive media from reaching the surface, delays corrosion development, and reduces friction coefficient. However, the comprehensive performance of conventional phosphating film can be further improved. According to the research, the composite phosphating film has better performance than the conventional phosphating film. Polytetrafluoroethylene (PTFE) is a kind of polymer particle with excellent corrosion resistance and wear resistance [19-21]. To some extent, the PTFE particle doped into the phosphating film to considerably increase the phosphating film's overall qualities is novel. Therefore, in this paper, PTFE particles were introduced in the manganese phosphating process to prepare phosphating film called as manganese composite phosphating. The morphology, composition, thickness, corrosion resistance and wear resistance of the manganese composite phosphating film on the gear surface were characterized and analyzed.

2. EXPERIMENTAL

2.1 Chemical agents

The gear used in the experiment is made of 45 steel which contains 0.42~0.50% C, 0.50~0.80% Mn, 0.17~0.37% Si, 0.30% Ni, 0.25% Cr and Fe more than 98%. The reagents used are all analytical pure: sodium hydroxide, sodium carbonate, hydrochloric acid (37%), sodium chloride, manganese(II) hypophosphite, manganese nitrate, phosphoric acid (85%) and nickel nitrate.

2.2 Manganese composite phosphating treatment

The manganese composite phosphating treatment for gear in the experiment includes three steps.

Step 1: The surface of the gear was polished by a rubber grinding wheel to remove the oxide skin, and then soak it in hot alkali solution (45 g/L sodium hydroxide, 15 g/L sodium carbonate, 60°C) for 8 minutes to remove the oil completely. After that, the gear was activated by soaking in 15% hydrochloric acid for 1 minute. Finally, it was cleaned with deionized water and dried by a blower.

Step 2: Pretreatment solution with 4 g/L colloidal titanium was prepared firstly. And then, two cups of 1000 mL manganese phosphating solution with and without PTFE particles were prepared.

One is the manganese phosphating solution which is consisted of 40 g/L manganese(II) hypophosphite, 15 g/L manganese nitrate, 4 g/L phosphoric acid and 1.5 g/L nickel nitrate. The other is the manganese composite phosphating solution with 40 g/L manganese(II) hypophosphite, 15 g/L manganese nitrate, 4 g/L phosphoric acid, 1.5 g/L nickel nitrate and 16 ml/L PTFE emulsion. The PTFE emulsion is a water based dispersion of PTFE particles (particle size about 100 nm), of which the mass fraction of PTFE particles is about 70%.

Step 3: The polished gear is immersed into the pretreatment solution with 4 g/L colloidal titanium for 40 seconds at room temperature. After that, the gear is put into the manganese phosphating solution and manganese composite solution respectively for 20 minutes. In order to ensure better uniform dispersion of PTFE particles, the manganese composite phosphating solution is fully stirred at a rate of 150 r/min.

2.3 Testing

2.3.1 Surface morphology and composition

The appearance of gears was photographed by EOS 7D Mark II digital camera. The surface morphology of different manganese phosphating films on gears was observed by EV018 scanning electron microscope equipped with energy spectrometer, and the composition of manganese phosphating films was analyzed.

2.3.2 Thickness measurement

TT260 thickness gauge was used to measure the thickness of different manganese phosphating films on the surface of the gear. In order to reduce the measurement error, three points were selected at any point on the end face of the gear and the average value was calculated.

2.3.3 Electrochemical test

The polarization curves and electrochemical impedance spectra were measured by Parstat 2273 electrochemical workstation with saturated calomel electrode as reference electrode and platinum electrode as auxiliary electrode.

The surface of the gear was cut to square block of 1 cm×1 cm and polished. The copper wires were welded on the back of the gear and then sealed with epoxy resin, exposing only 1 cm×1 cm area.

The corrosion medium was 3.5% sodium chloride solution. Scanning rate of polarization curve kept at 1 mV/s and testing results were imported into PowerSuite software for fitting analysis. The scanning frequency of electrochemical impedance spectrum was 10^5~10^{-2} Hz, and the signal amplitude was 10 mV. The test results were imported into ZSimpWin software for fitting analysis.

2.3.4 Friction test

The gear friction experiment was carried out on the simulated transmission table, and two same gears were selected for meshing. The experimental conditions were as follows: no lubrication, rotation speed of 400 r/min and experimental period of 72 h. After the experiment, the wear morphology of gear surface was observed by scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1 Appearance of gear with and without manganese phosphating treatment

Figure 1(a) shows the appearance of untreated gear. It can be seen that the untreated gear is basically silvery white. Figure 1(b) shows the appearance of the gear after conventional manganese phosphating treatment. It can be seen that the gear is black after conventional manganese phosphating treatment, and the conventional manganese phosphating film is completely covered. Figure 1(c) shows the appearance of the gear after manganese composite phosphating treatment. It can be seen that the gear after manganese composite phosphating treatment is also black, and its appearance is not much different from that after conventional manganese phosphating treatment.

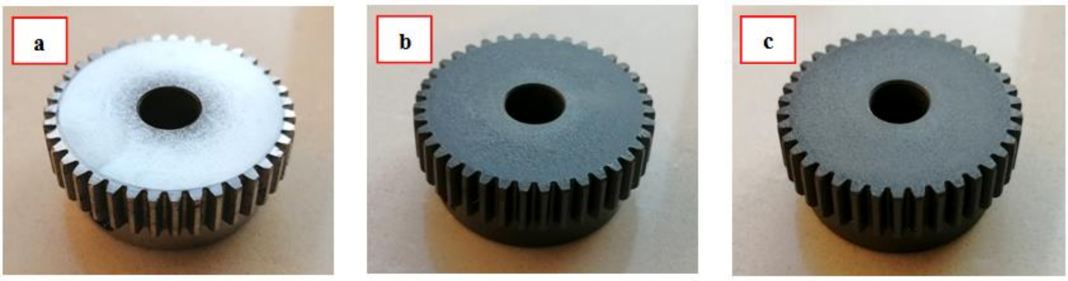


Figure 1. The appearance of gear with and without manganese phosphating treatment; a-untreated gear; b-the gear after conventional manganese phosphating treatment; c-the gear after manganese composite phosphating treatment; picture mode is auto focus without magnification

3.2 Morphology and composition of different manganese phosphating films on 45 steel surface

Figure 2 shows the morphology of 45 steel, conventional manganese phosphating film and manganese composite phosphating film. As can be seen from Figure 2, strip wear marks and tiny pits can be found on the surface of 45 steel, which are traces left by grinding. The grains of conventional manganese phosphating films are irregular polyhedral with size of 5~10 μm and closely bonded which is similar to the paper reported [22-26]. The grains of manganese composite phosphating film are also irregular polyhedral, but a large number of PTFE particles are attached to the surface of the grains and the gap between the grains. PTFE particles play a physical filling role, but have little effect on grain morphology, grain size and bonding state. The effect of PTFE doping is also reported in some literatures [27-30].

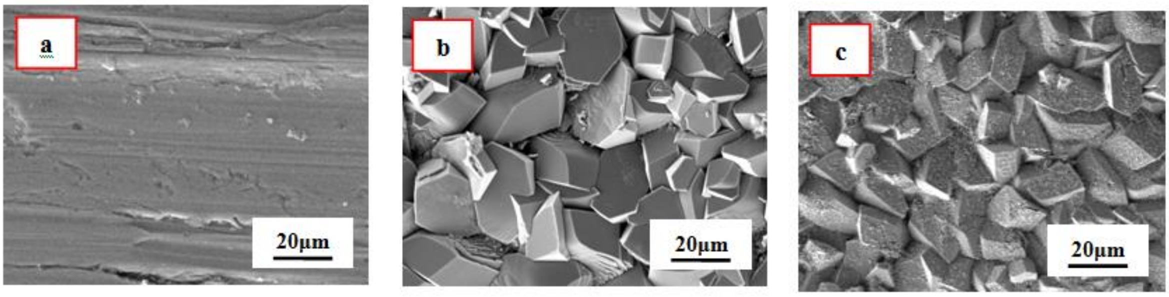
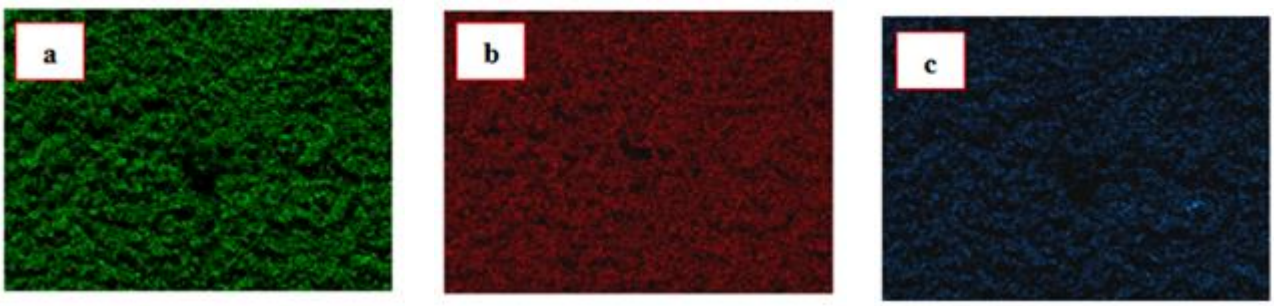


Figure 2. The surface morphology of different manganese phosphating films on 45 steel surface; a-45 steel; b-conventional manganese phosphating film; c-manganese composite phosphating film; sample size 8 mm×8 mm×2 mm; magnification 900 times; accelerating voltage 10 kV

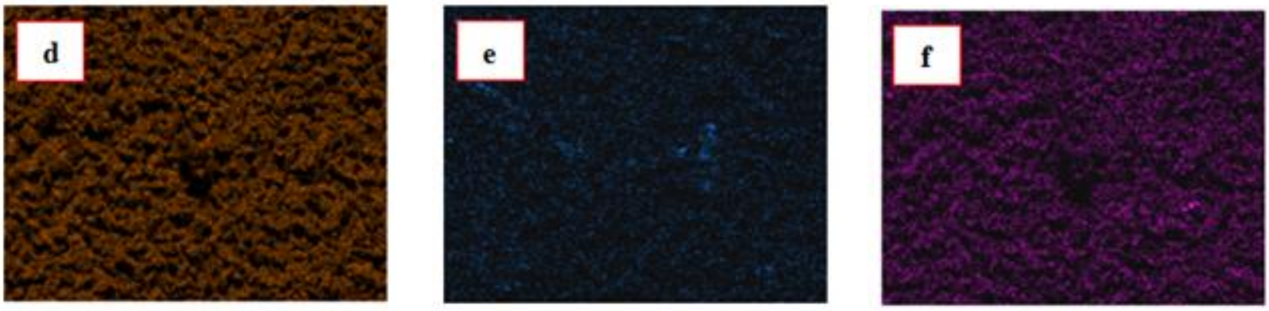
Table 1 shows the EDS analysis results of conventional manganese phosphating film and manganese composite phosphating film. As can be seen from Table 1, conventional manganese phosphating film is mainly composed of Mn, P, Fe and O elements which are close to results reported by others [31-33]. Meanwhile, the mass fraction of O element is the highest, reaching 44.26%. Manganese composite phosphating film is mainly composed of Mn, P, Fe, O, C and F elements. Compared with conventional manganese phosphating film, there are more C and F elements in manganese composite phosphating film. These two elements are characteristic elements of PTFE[$(C_2F_4)_n$].

Table 1. Elements distribution of different manganese phosphating films on 45 steel surface

Samples	**Element mass fraction/ %**					
	Mn	**P**	**Fe**	**O**	**C**	**F**
conventional manganese phosphating film	30.12	20.58	5.04	44.26	—	—
manganese composite phosphating film	26.48	18.19	6.63	39.09	5.46	4.15



(a) Mn element distribution (b) P element distribution (c) Fe element distribution



(d) O element distribution (e) C element distribution (f) F element distribution

Figure 3. Distribution of elements on the surface of manganese composite phosphating film; accelerating voltage 10 kV; surface sweep model; sampling depth 1 μm

Figure 3 shows the distribution of elements on the surface of manganese composite phosphating film. It is found out that Mn, P, Fe, O, C and F elements are evenly distributed, indicating that the PTFE particles in the manganese composite phosphating film are in a dispersion state without obvious agglomeration phenomenon. According to the mass fraction of F element, the content of PTFE particles in the manganese composite phosphating film is about 5.46%.

3.3 Thickness of different manganese phosphating films on 45 steel surface

Table 2 shows the thickness measurement results of conventional manganese phosphating film and manganese composite phosphating film on 45 steel surface. According to Table 2, the uniformity of conventional manganese phosphating film and manganese composite phosphating film is both good, and the thickness is basically the same, about 13 μm. It verifies that PTFE particles have little effect on the thickness of manganese phosphating film.

Table 2. Thickness of different manganese phosphating films on 45 steel surface

Samples	Value 1	Value 2	Value 3	Average
conventional manganese phosphating film	13.2 μm	12.9 μm	13.3 μm	13.1 μm
manganese composite phosphating film	13.4 μm	13.2 μm	13.1 μm	13.2 μm

3.4 Corrosion resistance of different manganese phosphating films on 45 steel surface

3.4.1 Electrochemical test results

Figure 4 shows the polarization curves of 45 steel, conventional manganese phosphating film and manganese composite phosphating film. As can be seen from Figure 4, the polarization curves of both conventional manganese phosphating film and manganese composite phosphating film shift to the lower right compared with those of 45 steel, indicating that the corrosion potential shifts positively and the corrosion current density decreases. As can be seen from Table 3, the corrosion potential of 45 steel is -510 mV. The corrosion potential of conventional manganese phosphating film and manganese composite phosphating film moves to -471 mV and -446 mV respectively. The corrosion current density of 45 steel is 6.17×10^{-5} A/cm^2, while the corrosion current density of conventional manganese phosphating film and manganese composite phosphating film is reduced to 3.64×10^{-6} A/cm^2 and 1.93×10^{-6} A/cm^2, respectively. It has been proved by some researches that phosphating film has good corrosion resistance and can effectively slow down the corrosion process [34-38]. The grain gaps of manganese composite phosphating film contain many PTFE particles, and the PTFE is stable and nonconducting with higher impedance. Therefore, a large amount of PTFE particles could help block the penetration of corrosive medium to reduce corrosion tendency resulting in the decrease of corrosion current density.

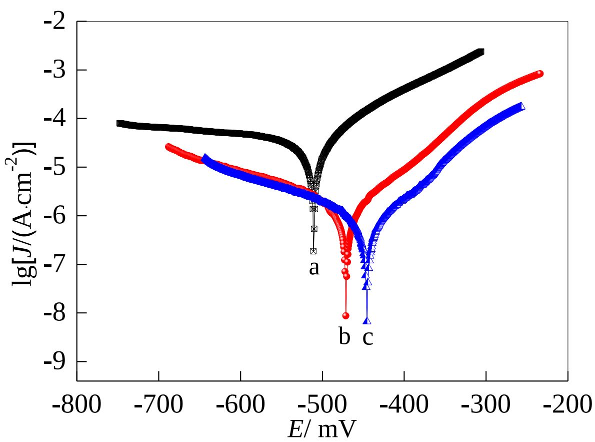


Figure 4. Polarization curves of different manganese phosphating films on 45 steel surface; a-45 steel; b-conventional manganese phosphating film; c-manganese composite phosphating film; saturated calomel electrode as reference electrode and platinum electrode as auxiliary electrode; different manganese phosphating film sample as the working electrode; the corrosion medium was 3.5% sodium chloride solution; scanning rate of polarization curve is 1 mV/s

Table 3. Fitting results of polarization curves

Samples	Corrosion Potential/ mV	Corrosion current density/ (A/cm^2)
45 steel	-510	6.17×10^{-5}
conventional manganese phosphating film	-471	3.64×10^{-6}
manganese composite phosphating film	-446	1.93×10^{-6}

Figure 5 shows the electrochemical impedance spectra of 45 steel, conventional manganese phosphating film and manganese composite phosphating film. The impedance spectrum radius of 45 steel, conventional manganese phosphating film, and manganese composite phosphating film increases sequentially, as shown in Figure 5. The impedance spectrum radius of manganese composite phosphating film is the largest, showing better corrosion resistance.

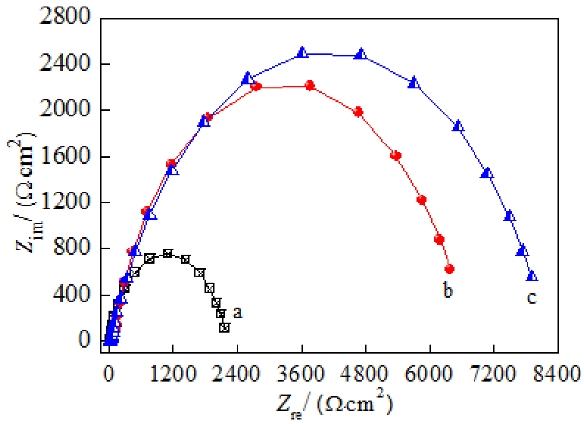


Figure 5. Electrochemical impedance spectra of different manganese phosphating films on 45 steel surface; a-45 steel; b-conventional manganese phosphating film; c-manganese composite phosphating film; saturated calomel electrode as reference electrode and platinum electrode as auxiliary electrode; different manganese phosphating film sample as the working electrode; the corrosion medium was 3.5% sodium chloride solution; scanning frequency of electrochemical impedance spectrum was 10^5~10^{-2} Hz, and the signal amplitude was 10 mV

Table 4 shows the fitting results of electrochemical impedance spectrum, in which the resistance of film layer can reflect the blocking effect of manganese phosphating film on corrosive medium. The charge transfer resistance reflects the difficulty of charge transfer at the interface between manganese phosphating film and corrosive medium.

Table 4. Fitting results of electrochemical impedance spectrum

Samples	**Film resistance/ (Ω·cm^2)**	**Charge transfer resistance/ (Ω·cm^2)**
45 steel	315.2	2048.6
conventional manganese phosphating film	950.5	6178.3
manganese composite phosphating film	1193.0	7754.5

The film resistance and charge transfer resistance of the conventional manganese phosphating film are 950.5 Ω·cm^2 and 6178.3 Ω·cm^2 respectively, which prove that the conventional manganese phosphating film has strong resistance to corrosive media and can effectively slow down the corrosion of 45 steel. However, manganese composite phosphating film of film resistance and the charge transfer resistance is larger than conventional manganese phosphating film. It means that the manganese composite phosphating film can better stop the corrosion process and extend the penetration of the corrosive medium, so as to show the best corrosion resistance.

3.4.2 Salt spray test results

Figure 6 shows the appearance of untreated gear, the gear after conventional manganese phosphating treatment and the gear after manganese composite phosphating treatment after 48 hours salt spray testing. As can be seen from Figure 6(a), large areas of corrosion appeared on the surface which is yellow brown and loose corrosion products. According to Figure 6(b) and Figure 6(c), the corrosion areas of the manganese based phosphating gear and composite phosphating gear are smaller, and the corrosion degree is significantly reduced. In particular, there are only a few corrosion points on the surface of the gear after the manganese based composite phosphating treatment. The PTFF particles attached to the crystal surface and filled into the gap, play a good physical shielding role to prevent the penetration of corrosive medium and delay the corrosion process resulting in better corrosion resistance performance.

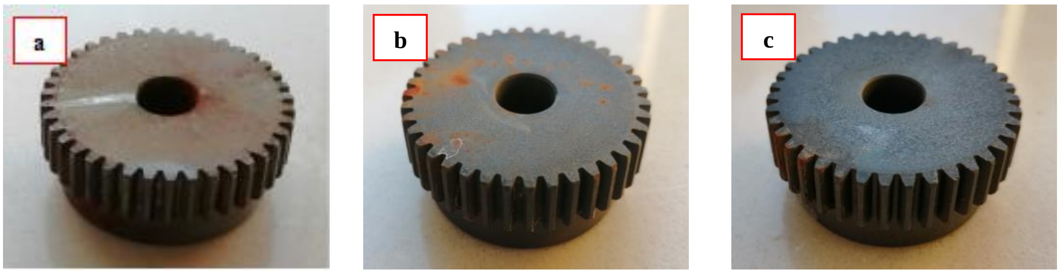


Figure 6. The appearance of gear with and without manganese phosphating treatment after 48 hours salt spray testing; a-untreated gear; b-the gear after conventional manganese phosphating treatment; c-the gear after manganese composite phosphating treatment; picture mode is auto focus without magnification

3.5 Wear resistance of different manganese phosphating films on 45 steel surface

Figure 7 shows the wear morphology of 45 steel, conventional manganese phosphating film and manganese composite phosphating film. It can be seen from Figure 7(a) that the surface of 45 steel is severely worn and many fine granular and large block chips are observed, which is caused by serious cutting wear. However, the surface wear degree of conventional manganese phosphating film is reduced, but there are still obvious scratches and cracks found on the surface. It can be seen from Figure 7(c), the surface wear degree of manganese composite phosphating film is the lightest. Because the PTFE particle possesses self lubrication performance and is not sticky, the PTFE distribution on the surface of grain and grain gaps will form a layer of solid lubricating film during wearing process to greatly reduce the friction coefficient and wear rate.

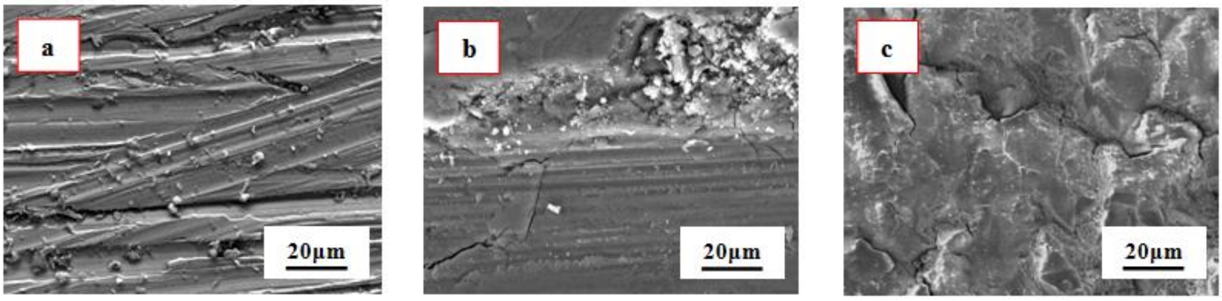


Figure 7. The wear appearance of different manganese phosphating films on 45 steel surface; a-45 steel; b-conventional manganese phosphating film; c-manganese composite phosphating film; sample size 8 mm×8 mm×2 mm; magnification 900 times; accelerating voltage 10 kV

4. CONCLUSIONS

Phosphating technology was used to prepare manganese phosphating film on the surface of gear to extremely improve the corrosion resistance and wear resistance performance to meet the requirement of industry applications. The conclusions are as follows:

(1) The appearance of the gear treated with manganese phosphating or manganese composite phosphating treatment is almost the same, showing dark. Moreover, many irregular polyhedral with micron sizes were observed on the surface of conventional manganese phosphating film and manganese composite phosphating film. However, manganese composite phosphating film contains many PTFE particles on the grains and the gaps between the grains which play a physical filling role.

(2) The gear treated with manganese composite phosphating has the best corrosion resistance and wear resistance due to larger amount of PTFE particles doping on the grains and gaps. PTFE particles has self lubrication performance with higher impedance which could block the penetration of corrosive medium and form a layer of solid lubricating film to greatly reduce corrosion and wear.

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