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Effect of phosphating time and temperature on microstructure and corrosion behavior of magnesium phosphate coating

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A B S T R A C T

In this study a novel phosphate coating, magnesium phosphate, was developed on steel surface. The formation of the coating was confirmed by X-ray diffraction method. Morphological evolution of the coating, as a function of phosphating time and temperature, was examined by scanning electron microscope. Magnetic thickness gauge was used to determine the thickness of the coating and the bath sludge weight was specified to determine the bath efficiency. Corrosion behavior of the samples was studied using potentiodynamic polarization curves. The results indicated that increasing the phosphating temperature facilitated the precipitation of coating and increased its thickness. Furthermore the best corrosion behavior was observed at 80 °C. Also increasing the phosphating time, enhanced both thickness and uniformity of the coating. The best results were observed after 20 min of phosphating.

1. Introduction

Carbon steels are widely used in various industries, due to their high strength, good hardness and proper toughness, but their low corrosion resistance limits their application in some cases. Phosphating is one of the most important processes, applied to steels, especially in automotive industries, to improve their corrosion resistance, paintability and lubrication properties [1–3]. Phosphate coatings are usually applied on carbon steel, galvanized steel, magnesium, aluminum and zinc, but in some cases when improving the paintability is required they are also applied on stainless steels [4–7]. Zinc, manganese and iron phosphate coatings are the most common types of these coatings [8–13]. Lots of research has been done to reach a good corrosion resistance in phosphate coatings. Using a double cationic phosphate coatings, post sealing of the coating with molybdate or some other compounds and using additives, such as copper ions and ethanolamine have shown to be effective for improving the corrosion resistance of these coatings [14–18]. The type and amount of accelerators has also shown to play an important role in coating quality [9,19]. Several parameters affect the corrosion resistance of a coating, e.g. thickness of coating, its porosity and the microstructure. It has shown that increasing the thickness of coating and decreasing its porosity, results in better corrosion resistance [20,21]. One of the problems of the prevalent phosphate coatings such as zinc and manganese phosphate coatings is their

low thickness. The normal thickness of zinc phosphate coating is less that 10 μm and for manganese or zinc–manganese phosphate coating can reach 20 μm [14]. So it seems necessary to find a way to increase the thickness of these coatings. Therefore developing a novel phosphate coating with different chemical composition can be effective. Although some research has been done to develop third and secondary magnesium phosphate on steel and magnesium respectively [22,23], but developing the secondary magnesium phosphate on steel was never been studied. So in this study, novel secondary magnesium phosphate coating is developed on steel surface to improve its efficiency.

2. Experimental procedure

Mild steel sheets (50 mm × 40 mm × 1 mm) were used as the substrate. Chemical composition of the substrate is given in Table 1. The sheets were degreased in 10 wt.% NaOH solution at 60 °C for 5 min. Abrading procedure was performed by 400 grit emery paper. Then the samples were rinsed with acetone and deionized water to remove any remaining grease from the surface. Afterwards the samples were acid pickled using 10 wt.% H_2SO_4 solution at 60 °C for 3 min to provide a proper base for nucleation of the phosphate coating. They were then rinsed with deionized water again and finally they were immersed in 350 mL volume of magnesium phosphate bath with the composition, mentioned in Table 2. To study the effect of phosphating time, the samples were phosphated for 1, 3, 5, 10, 20 and 30 min while the temperature was stayed constant at 80 °C. Also to study the effect of phosphating temperature, the phosphating time was stayed constant at 20 min and phosphating was studied at 25 °C, 40 °C, 60 °C, 80 °C and 90 °C. Formation of

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Table 1
The composition of steel substrate (wt.%).

Fe	C	Si	Mn	P	S	Ni	Al	Mo	Cu
Balance	0.02	0.01	0.21	0.007	0.006	0.02	0.054	0.01	0.004

Table 2
Chemical composition of magnesium phosphate bath.

Concentration	Bath composition
23 mL/L	H_3PO_4 (85%)
8.5 g/L	$MgCO_3$
0.4 g/L	$NaNO_2$
6.8 g/L	NaOH

the coating was confirmed by X-ray diffraction method. Scanning electron microscope was used to study the coating microstructure. A magnetic thickness gauge was used to determine the coating thickness. The results are the average of 5 measurements.

The sludge amount which precipitated in the bath after the process was separated using a filter paper and weighed in order to determine the bath efficiency factor [22]. Bath efficiency factor can be defined by Eq. (1). It defines a criterion of effectiveness of the bath by changing different parameters, i.e. by increasing the coating thickness and decreasing the sludge weight, the bath efficiency would be enhanced.

$$\text{bath efficiency} = \frac{\text{thickness of coating}}{\text{sludge weight}} \qquad (1)$$

Potentiodynamic polarization tests were performed by suspending the samples in 3.5 wt.% NaCl solution. The counter and reference electrodes were platinum and Saturated Calomel Electrode (SCE), respectively. After about 1 h of stabilization at rest potential, polarization test commenced at a scan rate of 2 mV/s using an EG&G273 potentiostat instrument. To check the reproducibility of the tests, each sample was tested three times. Finally the corrosion rate was calculated using Eq. (2) [24,25]:

$$\text{corrosion rate} = 0.326 \times 10^{-2} \left(\frac{i_{\text{corr}} M}{ZD} \right) \qquad (2)$$

where i_{corr} is the corrosion current density, M is the molecular weight, D is the density of metal and Z is the metal capacity in oxidation state. The coating porosity percentage was also calculated according to Eq. (3) [26,27]:

$$P = \frac{R_{ps}}{R_p} \times 10^{-(\Delta E_{\text{corr}}/\beta_a)} \times 100 \qquad (3)$$

where P is the total coating porosity percentage, R_{ps} is the polarization resistance of bare substrate, R_p is the polarization resistance of coated substrate in, ΔE_{corr} is the difference between free corrosion potentials of coated and bare substrate, and β_a is the anodic Tafel slope of the substrate. Furthermore corrosion protection efficiency was calculated according to Eq. (4) [15]:

$$P_e\% = \left(1 - \frac{i_{\text{corr}}}{i_{\text{corr}}^0} \right) \times 100 \qquad (4)$$

where P_e is the corrosion protection efficiency of the coating, i_{corr} and i_{corr}^0 are corrosion current density of coated sample and the substrate, respectively.

3. Results and discussion

3.1. Phase analysis

X-ray diffraction pattern of the sample (Fig. 1) illustrates that the coating formed on steel substrate is a single phase coating,
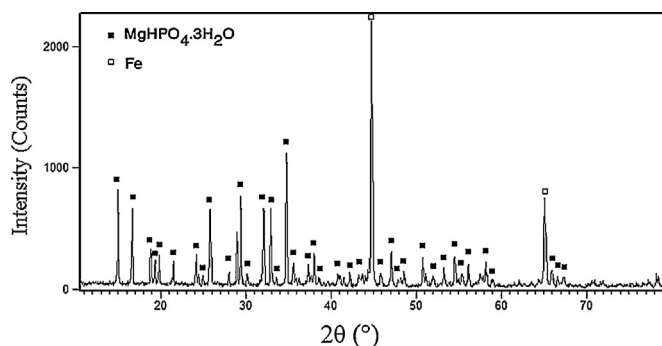

Fig. 1. XRD patterns of magnesium phosphate coating.

called newberyite, with the chemical formula of $MgHPO_4 \cdot 3H_2O$. This material is also known as magnesium phosphate dibasic and magnesium hydrogen phosphate. In XRD patterns all of the peaks are related to newberyite except the two at $2\theta = 44.76°$ and $65.16°$ which relate to iron and originates from steel substrate. The existence of these two peaks is because of the penetration of X-ray to the substrate.

XRD pattern of the bath sludge, shown in Fig. 2, indicates that the sludge is mostly consisted of amorphous compounds. There are also some crystalline compounds in the sludge but it is not possible to determine their composition due to the amorphous background. Meanwhile it is obvious that the sludge does not include a considerable amount of newberyite phase. So it declares that the sludge consists of some materials other than newberyite and much formation of sludge, means that the reactions do not shift toward the formation of newberyite. The other possibility is that some amount of newberyite which were not able to gain the substrate would precipitate as sludge in the bath and therefore it would decrease the bath efficiency too.

3.2. Formation mechanism

The reactions which lead to formation of newberyite can be as follows [28]:
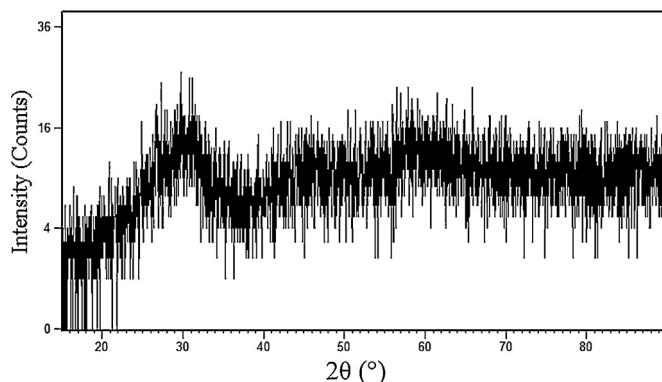

Fig. 2. XRD pattern of the sludge, precipitated from magnesium phosphate bath.