

Phosphatation of Iron Powder Metallurgical Samples for Corrosion Protection

H. Ashassi-Sorkhabi*, D. Seifzadeh and H. Harrafi

Electrochemistry Researches Laboratory, Department of Physical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

(Received 28 July 2006, Accepted 20 October 2006)

Recently, powder metallurgy methods have been used widely for industrial purposes. In this work, powder-metallurgically produced samples were selected for zinc phosphate coating. Zinc phosphate coating was performed at 50 and 70 °C for 20 min in a bath containing 10 g l⁻¹ ZnO, 25.5 g l⁻¹ H₃PO₄, 5.88 g l⁻¹ HNO₃, and 2 g l⁻¹ NaNO₃. The effect of temperature on the phosphating process has been studied. The structure and corrosion resistance of coats have been investigated using scanning electron microscopy (SEM) and electrochemical methods (polarization and EIS). Results show that an increase in temperature affects the crystalline structure of the coats. The formation of the zinc phosphate coat on the powder metallurgical samples significantly decreases the corrosion rate of the samples.

Keywords: Powder metallurgical sample, Zinc phosphate, Corrosion protection

INTRODUCTION

Powder metallurgical materials have been widely used in airplanes, trains and automobiles. The commonly used powder metallurgical materials are primarily Fe- and Cu-based, prepared by pressing and sintering metal powders with the addition of lubricants and friction particles. Fe-based materials have high friction coefficients, good heat resistance and low cost. In recent years, the speed and load of engineering machines have increased greatly, which increases the requirements for powder metallurgical products [1-3].

Phosphating is necessary to protect powder metallurgical samples from corrosion. The most commonly used phosphate coatings for corrosion protection are based on zinc, iron, and manganese, found in primer paint and electrical insulation. Generally, these compounds have the advantages of low cost,

simple processing and satisfactory protection [4]. The phosphate coat is formed by the chemical reaction that takes place after immersing the metal in a solution containing soluble primary metal phosphate, free phosphoric acid, various accelerators and modifiers [5]. The phosphatation of zinc, electro-galvanized steel, steel, and aluminum are well-known processes [6]. There are no reports in the literature about the phosphating of powder metallurgical samples.

The aim of this study is to determine the effectiveness of corrosion protection by the phosphatation of iron powder metallurgical samples evaluated by electrochemical methods including polarization and electrochemical impedance spectroscopy (EIS). In addition, scanning electron microscopy (SEM) and energy dispersive microscopy (EDX) spectrum were used to study the crystalline structure of the phosphate coatings.

*Corresponding author. E-mail: ashassi@tabrizu.ac.ir

EXPERIMENTAL

Samples

Iron powder metallurgical samples, made in Tabriz Powder Metallurgy Company (TPMCO), were selected for zinc phosphating. The samples were mounted in polyester in such a way that the area exposed to solution was 0.78 cm². They were polished using 800, 1200, 2500, grade emery paper, and degreased with acetone. Finally, the samples were washed out in flowing tap water and distilled water, respectively, and then dried using airflow at room temperature.

Phosphating Bath

Different bath compositions were examined in this work and the optimum bath composition used for the experiment consisted of 25.5 g l⁻¹ phosphoric acid, 5.88 g l⁻¹ nitric acid, 10 g l⁻¹ zinc oxide, and 2 g l⁻¹ sodium nitrate as an accelerator. Phosphating was performed in 300 ml of the bath solution at 50 and 70 °C for 20 min. The temperature was automatically kept at 50 and 70 °C ± 0.1 °C using a thermostat (Memmert, Germany). During the phosphating, the bath solution was stirred slowly to reduce the concentration polarization.

Electrochemical Measurements

To determine the corrosion resistance of coated and uncoated powder metallurgical samples, electrochemical experiments were carried out in a corroding solution of 3% NaCl prepared using de-ionized water. A computer-controlled Autolab PGSTAT 30 was used for potentiodynamic polarization and electrochemical impedance studies. This system employed a three-component cell consisting of an Ag/AgCl (3 M) electrode as the reference electrode, a platinum electrode (0.5 cm² surface area) as the counter electrode and the iron samples as a working electrode. EIS measurements were performed at the open circuit potential by applying an AC signal (10-mV sine wave) in a frequency range of 100 KHz-0.005 Hz. The uncoated and coated iron powder metallurgical samples were immersed in 3% NaCl for 30 min, after which Nyquist plots were obtained.

For polarization measurements, the potential was scanned in the cathodic-anodic direction, so that the maximum overvoltage was ±100 mV with a scan rate of 0.5 mV s⁻¹. The samples were immersed for 0.5 h in corroding solution, after which polarization curves were obtained. Corrosion parameters were obtained using the GPES software.

Surface Analyses

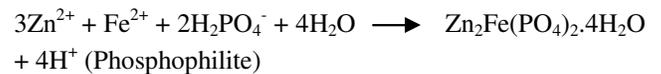
The morphology and the coating compositions were studied by SEM and EDX. Observations were made before and after the immersion of the samples in the phosphating bath.

RESULTS AND DISCUSSION

Phosphatation

As seen in the SEM images (Figs. 1 and 2), the zinc phosphate layer was formed on the iron powder metallurgical samples and the grain size of phosphate crystals strongly decreased as the phosphatation temperature increased. This reduction in grain size aids the formation of a more uniform zinc phosphate coating with higher corrosion resistance [7]. Also, the EDX spectra show that the amount of Zn, Fe, or P in the phosphate layer increases as the temperature increases, helping to form a heavier phosphate coating at 70 °C.

Typically, the zinc phosphate crystals form as two different structures [8]:



In many cases, both chemical forms exist in the phosphate coating in various percentages. Some parameters, such as the pretreatment method and temperature, can alter the chemical composition of the zinc phosphate coating. The general consensus is that the slow bath reaction causes an increase in the amount of iron-zinc phosphate (phosphophilite) [8]. It is obvious from the EDX spectra (Figs. 2a and 2b) that the increase in phosphating temperature causes an increase in the phosphating reaction rate and a decrease in the amount of phosphophilite in the coat.

Evaluation of Corrosion Resistance of Phosphated Samples

Potentiodynamic polarization. The polarization curves in Fig. 3 and corresponding data in Table 1 show that the corrosion rate of the uncoated iron samples is very high,

Phosphatation of Iron Powder Samples for Corrosion Protection

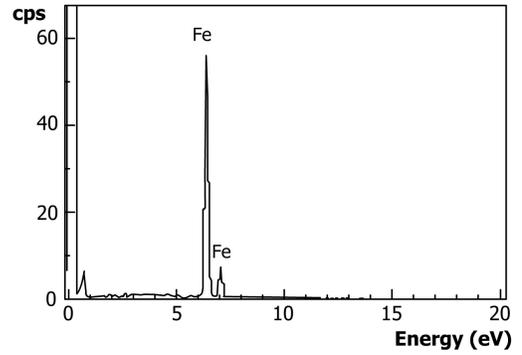
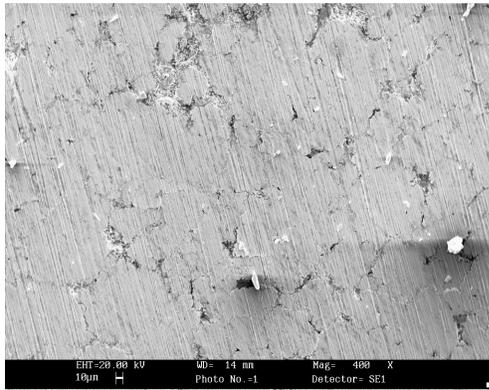
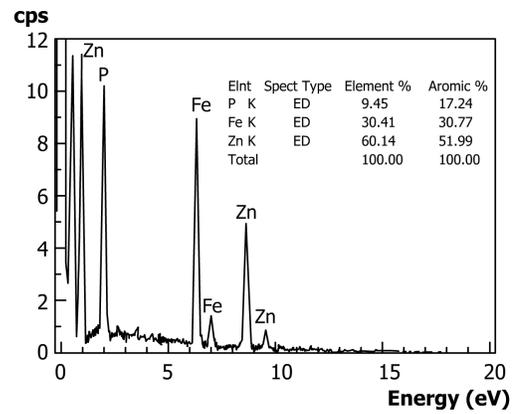
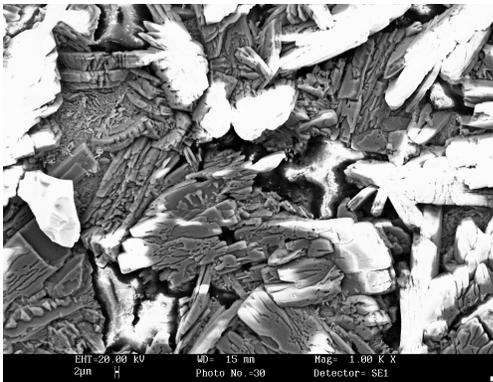
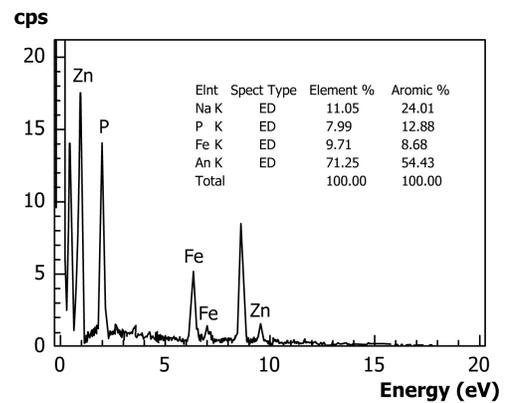
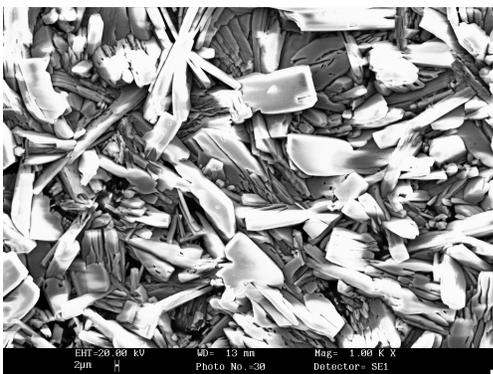


Fig. 1. SEM image and EDX spectrum of the uncoated powder metallurgical sample.



a



b

Fig. 2. SEM images and EDX spectra of the zinc phosphated powder metallurgical samples: a) 50 °C, b) 70 °C.

demonstrating the necessity for corrosion protection for these samples. Furthermore, the corrosion rate of the powder metallurgical samples is greatly reduced after the phosphating process.

The insulating property of the phosphate coating contributes significantly toward reduction of corrosion. As an insulator, the phosphate coating is not directly engaged in any electrochemical reaction. In the corrosion process, the metal, solution and interface create an electric circuit from the cathodic to the anodic sites. According to Ohms law, the corrosion rate depends on the total resistivity of the circuit. Compared to an electrically conductive coating, the phosphate layer obviously increases the circuit resistivity. As the anodic and cathodic processes can only continue at the metal surface

within the pores of the coating, transportation of reactant and corrosion products through the coating are also obstructed [4]. In the NaCl solution, the anodic and cathodic half-cell reactions of the corrosion process are the oxidation of metal and reduction of oxygen, respectively. Due to the low conductivity of the phosphate coat, the reduction of oxygen cannot take place. Therefore, both anodic and cathodic processes are hindered by the phosphate coating.

The corrosion resistance of the coating increases with phosphating temperature, which is explained by the increase in the phosphating reaction rate, coating weight and its thickness at higher temperatures. As seen from the EDX spectra, the amount of Fe in the coat decreases with an increase in temperature from 50 to 70 °C. This may also be

Table 1. Corrosion Parameters for Uncoated and Coated Samples in 3% NaCl

Sample	Phosphating temperature (°C)	R_p (Ω)	I_{corr} (A)	r_{Corr} (mmyr ⁻¹)
Uncoated	-	686	1.04×10^{-4}	1.21
Phosphated sample	50	1875	5.86×10^{-5}	6.64×10^{-1}
	70	2427	2.86×10^{-5}	3.34×10^{-1}

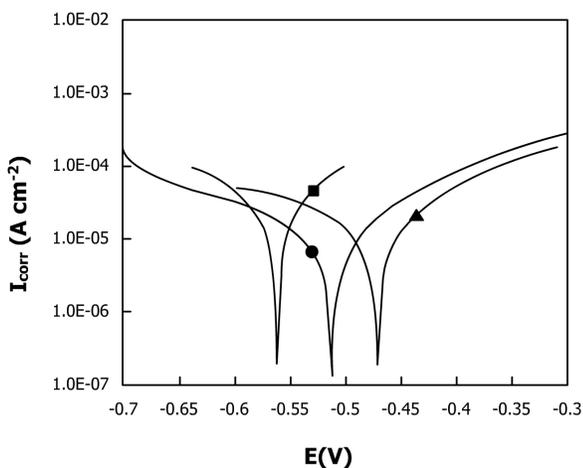


Fig. 3. Polarization curves of uncoated and phosphated samples in different temperatures in 3% NaCl: (■) uncoated sample, (▲) coated in 50 °C, (●) coated in 70 °C.

due to masking of Fe from the substrate by a thicker coating [4].

EIS studies. The Nyquist plots of the uncoated and coated iron powder metallurgical samples are shown in Fig. 4. Compared to the substrate, in 3% NaCl the polarization resistance of the zinc phosphated samples significantly increases, i.e. the corrosion resistance of the phosphate-coated sample is better than that of the uncoated sample. The effect of temperature on the phosphating reaction is the same as in polarization studies. The Nyquist plot of the uncoated sample consists of only one semicircle; thus an equivalent circuit model (Fig. 5a), with one time constant for the plot analysis can be used. The EIS data were fitted to a corresponding electrical circuit model using Zview version 2.3f (P.5), as shown in Table 2. R_{ct} is the charge transfer resistance and has a relatively small value, i.e. the corrosion rate of the samples is high. In many cases, the EIS spectra obtained did not exhibit

Phosphatation of Iron Powder Samples for Corrosion Protection

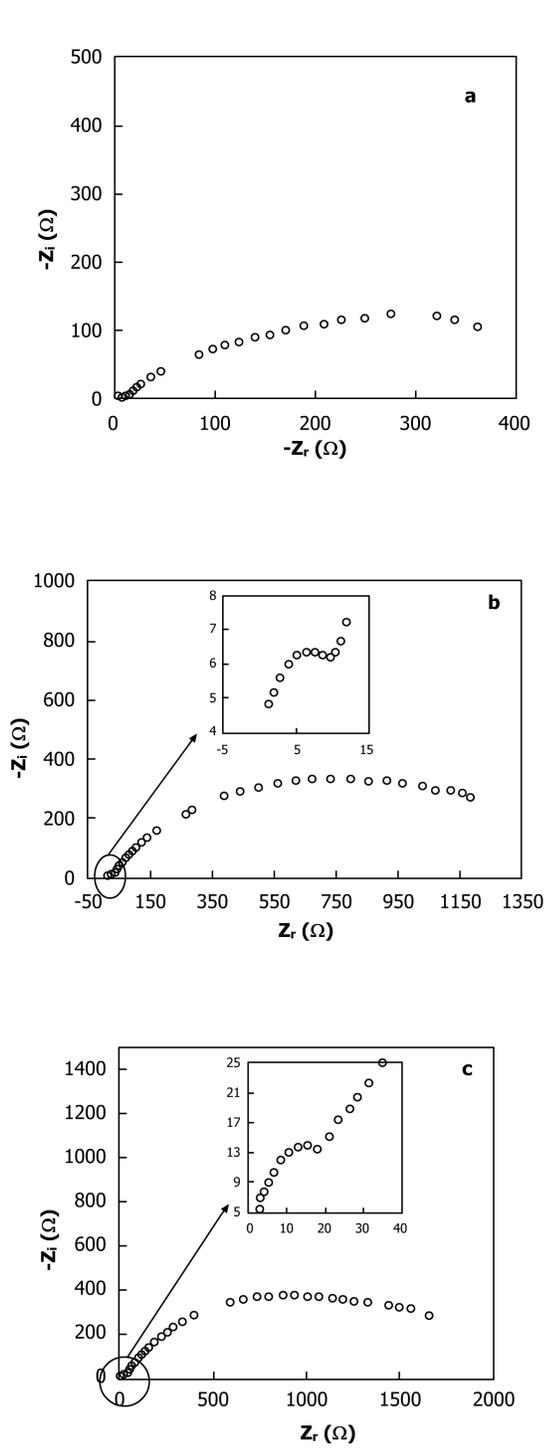


Fig. 4. The Nyquist plots of uncoated and zinc phosphated powder metallurgical samples in 3% NaCl: a) uncoated, b) phosphated at 50 °C, c) phosphated at 70 °C.

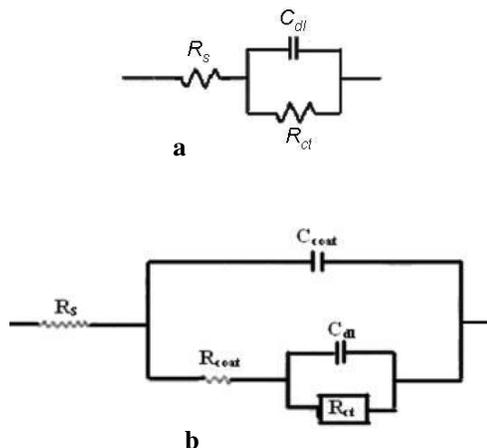


Fig. 5. Equivalent circuits for iron powder metallurgical samples in 3% NaCl, a) uncoated sample, b) zinc phosphated samples.

the straightforward behavior predicted using equivalent circuits with ideal electric elements [9]. Fracture of rough surfaces is the most common cause of frequency-dependent constant-phase elements (CPE) [5]. A CPE may arise from diffusion to a fractal surface or an irreversible electrode process and has been used to estimate the surface roughness [11-13].

The Nyquist plot with two capacitive loops is characteristic of a coated metal, one in the high frequency range and the other in the low frequency range. The first loop characterizes the coating layer and the second one indicates the charge transfer through the coating pores [14]. For these phosphated samples, the low frequency semicircle is clearer than the high frequency loop. However, the corrosion rates of the phosphated samples can be evaluated from the charge transfer resistance value taken from the low frequency measurements. An equivalent circuit model with two time constants (Fig. 5b) is used for analyzing the EIS plots. The fitting parameters are given in Table 3. Using the following equation, the corrosion protection efficiencies were calculated (Table 3).

$$\% \eta = (R_{ct} - R_{ct0}) / R_{ct}$$

From this it can be seen that the phosphate coating significantly protects the iron powder samples corrosion, and the increase in phosphating temperature promotes the effectiveness of this corrosion protection.

Table 2. EIS Parameters for the Uncoated Sample in 3% NaCl^a

Parameters	R_s (Ω)	R_{ct} (Ω)	C_{dl} (F)
	4.81	494	0.003649

^aObtained by Zview fitting program.**Table 3.** EIS Parameters for the Phosphated Samples in 3% NaCl^a

Sample	Phosphating temperature ($^{\circ}$ C)	R_{coat} (Ω)	C_{coat} (F)	R_{ct} (Ω)	C_{dl} (F)	η (%)
Zinc phosphated	50	17.24	2.51×10^{-5}	1377	6.27×10^{-4}	63.90
	70	24.67	3.47×10^{-7}	1854	4.81×10^{-4}	73.35

^aObtained by Zview fitting program.

CONCLUSIONS

The bath containing $25.5 \text{ g l}^{-1} \text{ H}_3\text{PO}_4$, $10 \text{ g l}^{-1} \text{ ZnO}$, $2 \text{ g l}^{-1} \text{ NaNO}_3$, and $5.88 \text{ g l}^{-1} \text{ HNO}_3$, is suitable for phosphating of iron powder metallurgical samples using the immersion method. SEM images and EDX analyses reveal that the structure and chemical composition of the zinc phosphate coating change with the change in phosphating temperature.

The electrochemical methods (polarization and EIS) show that the corrosion rate of iron powder metallurgical samples is strongly reduced after zinc phosphatation. Furthermore, both electrochemical investigations show that the increase in phosphating temperature increases the coating resistance against corrosion in 3% NaCl.

ACKNOWLEDGMENTS

The authors thank the Tabriz Powder Metallurgy Company for proposing the project, SUPCO (Iran Khodro) for financial support, and the Industrial Relations Office of Tabriz University.

REFERENCES

- [1] J. Li, Y. Yin, H. Ma, *Tribology International* 38 (2005) 159.

- [2] Y.L. Yang, *Sintering Metal Friction Materials, Mechanical Engineering Materials* 1995, pp. 18-21.
- [3] R.Z. Xu, *Powder Metallurgy Structural Materials, Changsha Publishing Company of Central South University of Technology*, 2002.
- [4] D. Weng, P. Jokiel, A. Uebleis, H. Boehni, *Surf. Coat. Technol.* 88 (1996) 147.
- [5] G. Bikulcius, V. Burokas, A. Martusiene, E. Matulionis, *Surf. Coat. Technol.* 172 (2003) 139.
- [6] L. Kouisni, M. Azzi, M. Zertoubi, F. Dalard, S. Maximovitch, *Surf. Coat. Technol.* 185 (2004) 58.
- [7] *Metals Hand Book*, 8th ed., Vol. 2, ASM Hand Book Committee, American Society of Metal, Metals Park, Ohio, 1964.
- [8] J. Donofrio, *Met. Finish.* 98 (2000) 57.
- [9] A. Loas, J.W. Schultz, *J. Electroanal. Chem.* 359 (1993) 39.
- [10] J.R. Macdonald, *Impedance Spectroscopy*, Wiley, New York, 1987.
- [11] A. Lemehaute, *J. Stat. Phys.* 36 (1984) 665.
- [12] A. Maritan, F. Toigo, *Electrochimica Acta* 35 (1990) 141.
- [13] G. Reinhard, U. Rammelt, *Metallober Flache* 42 (1988) 561.
- [14] P.B. Srinivasan, S. Sathiyarayanan, C. Markkannu, K. Balakrishnal, *Surf. Coat. Technol.* 64 (1994) 161.