

Effect of Chromium on the Corrosion Behavior of Powder-Processed Fe-0.6 wt% P Alloys

Yashwant Mehta*, Shefali Trivedi, K. Chandra, P. S. Mishra

Indian Institute of Technology, Roorkee, Uttarakhand, India

Email: *yashwant.mehta@gmail.com

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ABSTRACT

Phosphoric irons (*i.e.* Fe-P alloys containing low phosphorous in the range 0.1 to 0.7 wt%) with/without addition of chromium were prepared by powder forging route. The corrosion behaviour of these alloys was studied in different environments. The various environments chosen were acidic (0.25 M H₂SO₄ solution of pH 0.6), neutral/marine (3.5% NaCl solution of pH 6.8) and alkaline (0.5 M Na₂CO₃ + 1.0 M NaHCO₃ solution of pH 9.4). The corrosion studies were conducted using Tafel Extrapolation and Linear Polarization techniques. The results were compared with the corrosion resistance of electrolytic Armco iron. It was observed that, chromium improved the resistance to corrosion in marine conditions only. Corrosion rates were higher in acid medium due to the enhanced hydrogen evolution and hence, the cathodic reaction. The corrosion rates were minimal in alkaline medium and low in neutral solution.

Keywords: Phosphoric Iron; Alloy; Polarization; Acid Corrosion; Alkaline Corrosion

1. Introduction

Vera *et al.* reported that corrosion attack on plain carbon steel is more severe in a marine environment than in urban and rural media [1]. Fontana opines that corrosion of iron or steel is affected by environment [2]. Lorbeer and Lorenz found that corrosion depends on both, the composition of the metal/alloy and the environmental conditions. Important electrolyte variables affecting corrosion of iron are pH, concentration, fluid flow, temperature and oxidizing power of the solution [3]. Oxygen reduction predominates in weak acid and neutral solutions. Corrosion rate depends on hydrogen ion concentration in case of acidic solutions [3]. The addition of Chromium increased the atmospheric corrosion resistance in all the cases studied by Hudson and Stanners [4]. Segregation of phosphorus to grain boundaries can strongly affect intergranular stress corrosion cracking (SCC) of irons and steels in carbonate/bicarbonate solutions. This was reported by Parkins for irons [5] and Stencil *et al.* for steels [6]. Cleary and Greene said that phosphorus additions reduced alloy corrosion resistance and chromium did not affect the behaviour in de-aerated 0.1 N sulphuric acids [7].

Balasubramaniam writes that ancient phosphoric irons that were used for constructing large beams and located at Konark and Puri in India, have revealed excellent atmospheric corrosion resistance in saline seashore environments for several hundred years. The 1600-year-old

Delhi Iron Pillar displays exemplary corrosion resistance. The presence of 0.25 wt% phosphorus in the Pillar facilitates the formation of a protective passive film on the surface and thus provides excellent corrosion resistance to it [8,9]. Sahoo and Balasubramaniam found that Cr and Cu containing low alloy steel will be suitable for application in an acidic environment while alloying steel with phosphorus is not beneficial in such an environment [10].

An attempt therefore needs to be made to understand the role of chromium in carbon-free phosphoric irons. In this paper, the corrosion behavior of two powder metallurgy based phosphoric irons with 0.00 wt% C alloyed with/without chromium has been investigated in three different solutions.

2. Experimental

Iron powder (Fe-99.99 wt%, C-0.00 wt%; -200 mesh) was mixed with iron-phosphide (C-0.00 wt%; -200 mesh), low carbon ferro-chromium (C < 0.01 wt%; -200 mesh) to make the alloys by powder metallurgy. Iron and low carbon ferro-chromium powders were of commercial purity. Iron phosphide powder was prepared by mixing iron powders with ortho-phosphoric acid. The procedure of preparing iron-phosphide powder is described elsewhere [11]. Two powder metallurgical alloys were made in the present investigation. Their compositions are given in **Table 1**. The compositions of these alloys are based on the powder mixture. The process of making slabs by hot powder forging technique is explained elsewhere [11].

*Corresponding author.

Table 1. Composition of phosphoric irons developed in the study & Armco iron.

Sample	P (wt%)	Cr (wt%)	Fe
1 (Armco)	-	-	>99%
2	0.6	-	Balance
3	0.6	4	Balance

Samples for corrosion testing were prepared as detailed elsewhere [11]. The samples were mounted in a K0047 Corrosion Cell (used in ASTM standard G-5, supplied by Ametek, USA) for conducting Tafel polarization studies at a scan rate of 0.166 mV/s. The Tafel extrapolation method (conducted as per ASTM Standard G3-89 [12]) was utilized for determining i_{corr} of the phosphoric irons and Armco electrolytic iron in 3.5% NaCl having pH 6.8. Since the cathodic reaction was primarily diffusion controlled in the case of 3.5% NaCl solution having pH 6.8, the activation-controlled anodic Tafel region was extrapolated to intersect the horizontal drawn at zero current potential to obtain the corrosion rate as per ASTM Standard G102-89 [13].

Linear Polarization technique was used to evaluate the corrosion rates of the phosphoric irons in 0.5M Na₂CO₃ + 1.0 M NaHCO₃ solution of pH 9.4. A scan rate of 0.166 mV/s was used. Corrosion rate in penetration units (like mils/year, mpy), was calculated from i_{corr} using the following equation used by Ijselling [14]:

$$\text{mpy} = i_{\text{corr}} \times \Lambda \times 1 / \rho \times \varepsilon$$

where $\Lambda = 1.2866 \times 10^5$

(equivalents · s · mil)/(Coulombs · cm · years),

i_{corr} = the corrosion current density in Amps/cm² (Amp = 1 Coulomb/s),

ρ = density (7.86 g/cm³, for iron),

ε = equivalent weight (27.56 g/equivalent, for iron).

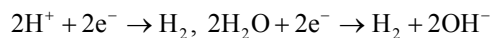
The solutions were prepared using chemicals of analytical grade reagent and single distilled water. A digital pH meter (Phillips, model 9045) was used for recording pH of the solutions at room temperature. The pH meter was calibrated using three different standard pH solutions before recording pH.

An EG and G PARSTAT 273A Potentiostat (Ametek, USA) and a saturated calomel reference electrode (SCE) were used in all electrochemical experiments. The open circuit potential (OCP) was stabilized for 1 hr before the start of each experiment. All the experiments were repeated three times.

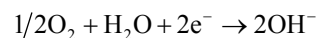
3. Results and Discussion

The corrosion rates determined by the Tafel extrapolation method in aerated solution of 0.25 M H₂SO₄ of pH 0.6 and 3.5% NaCl of pH 6.8 and those determined by the linear polarization method in aerated solutions of 0.5 M Na₂CO₃ + 1.0 M NaHCO₃ of pH 9.4 are discussed sepa-

rately below. Flitt and Schweinsberg said that the cathodic reaction for the samples obtained in all the three solutions discussed above consists of a composite reaction of [15] hydrogen evolution



and oxygen reduction



This is also evident from Pourbaix diagram of the Fe-H₂O system.

3.1. Tafel Extrapolation Method

3.1.1. 0.25 M H₂SO₄ Solution (pH 0.6)

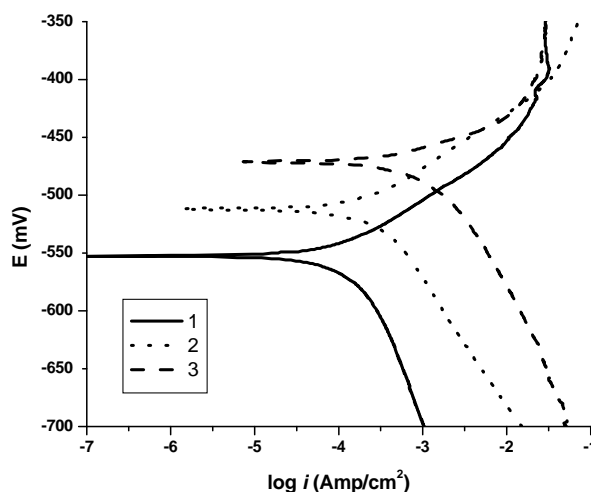
As pH decreases, hydrogen evolution rate tends to dominate over oxygen reduction rate at E_{corr} . Therefore, at pH 0.6, the contribution of hydrogen evolution at E_{corr} is noteworthy. The exchange current density i_0 for hydrogen evolution H⁺/H₂ and i_{corr} increase on increasing the concentration of H⁺ ion or decreasing the pH [16]. Hence corrosion rate increases.

The E_{corr} , i_{corr} and corrosion rate (mpy) obtained from the Tafel curves of the samples are tabulated in **Table 2** and displayed in **Figure 1**.

The E_{corr} lies between -471 mV_{SCE} and -511 mV_{SCE}. The corrosion rate for sample 2 is 152 mpy. This is less than that obtained for plain carbon steel (250 mpy) [10]. The corrosion rate for sample 3 is 1044 mpy.

Table 2. Corrosion data (Tafel) for Phosphoric irons in 0.25 M H₂SO₄ solution (0.6 pH).

Sample	E_{corr} vs SCE (mV)	I_{corr} (μA)	Corrosion Rate (mpy)
1	-553.0	174.7	78.8
2	-511.7	338.6	152.75
3	-471	2315	1044.36

**Figure 1. Tafel curves for Phosphoric irons in 0.25 M H₂SO₄ solution (0.6 pH).**

3.1.2. 3.5% NaCl Solution (pH 6.8)

The Tafel plots obtained in aerated 3.5% NaCl solution are shown in **Figure 2**. In this case, the diffusion controlled oxygen reduction reaction is the dominant reaction at E_{corr} [15]. The E_{corr} , i_{corr} and corrosion rate (mpy) obtained from the Tafel polarization curves of samples (**Figure 2**) are tabulated in **Table 3**.

The corrosion rate was obtained from the Tafel extrapolation method matched with literature data, as discussed below. The corrosion rate of iron is 12 mpy as obtained by McCafferty using the Tafel extrapolation method after 24 hours of immersion in unstirred, air saturated 3.5% NaCl solution [17]. Dexter reports that the actual corrosion rate of plain carbon steel (AISI 1020 steel) in quiet surface water is up to 15 mpy in the first year and then decreases to 5 mpy after 1000 days [18]. The E_{corr} of the samples lies between -600 mV_{SCE} and -690 mV_{SCE} . The corrosion rate of samples obtained by the Tafel extrapolation method after 1 h immersion in 3.5% NaCl was in the range of 6 to 10 mpy [10].

In the present study, the corrosion rate of samples obtained by the Tafel extrapolation method after 1 h immersion in 3.5 % NaCl was in the range of 1.3 to 7mpy. The E_{corr} of the samples lies between -619 mV_{SCE} and -633 mV_{SCE} .

3.2. Linear Polarization method

3.2.1. 0.5 M Na_2CO_3 + 1.0 M NaHCO_3 Solution (pH 9.4)

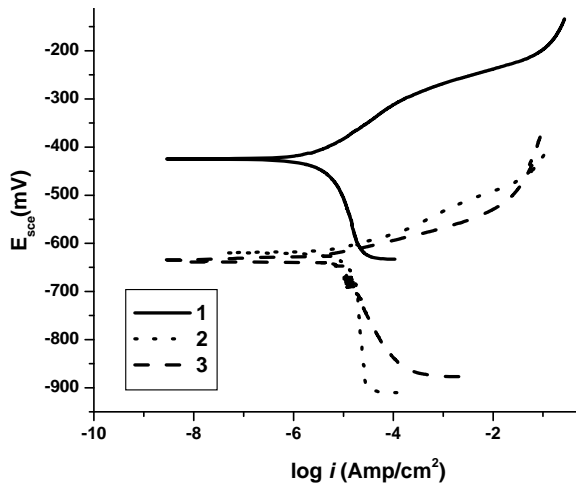


Figure 2. Tafel curves for phosphoric irons in 3.5% NaCl solution (6.8 pH).

Table 3. Corrosion data (Tafel) for phosphoric irons in 3.5% NaCl solution (6.8 pH).

Sample	E_{corr} vs SCE (mV)	i_{corr} (μA)	Corrosion Rate (mpy)
1	-424.6	2.897	1.3
2	-619.8	15.60	7.03
3	-633.8	2.958	1.33

This solution was chosen to evaluate the corrosion resistance of the samples against soil (buried condition). Sikora *et al.* reported that alkaline solutions are known to cause intergranular SCC due to segregation of Phosphorous in low alloy steels, [19].

The E_{corr} , i_{corr} and corrosion rate (mpy) obtained from the linear polarization curves of samples are tabulated in **Table 4** and displayed in **Figures 3(a)-(c)**. The E_{corr} lies between -250 mV_{SCE} and -262 mV_{SCE} . The corrosion rate is low and lies between 0.9 - 38 mpy (mils per year). The second composition can be used in buried (in soil) conditions.

3.3. Segregation of Alloying Elements

Powder metallurgical phosphoric irons developed in the present investigation are free of any segregation of the alloying elements along the grain boundaries. They get distributed uniformly in the entire structure. This has been confirmed by:

- Optical Microscope (**Figure 4**),
- Surface Morphology (SEM) and EDAX Pattern from different Spots (**Figures 5(a) and (b)**),
- Composition Image [Secondary Image] and X-Ray Mapping (**Figure 6**).

The optical micrographs show that the pores are elongated in the direction of rolling. The pores are found predominantly in the interior of the grains. The pores appear larger than their actual size due to the effect of etching. All the grains belong to a single phase that is ferrite. No other phase can be detected.

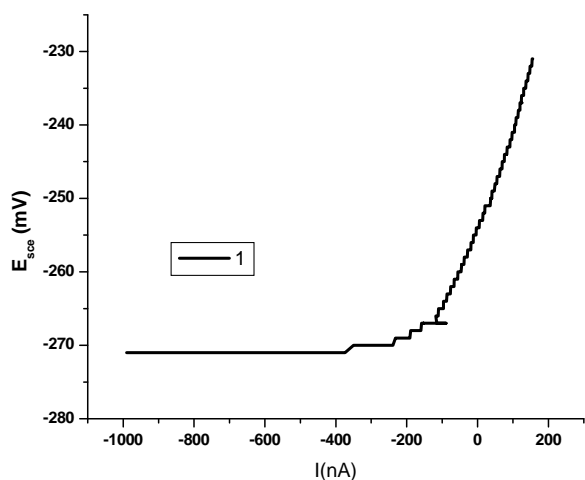
The SEM photos reveal that the grains are of a single phase. There is no second phase. The pores are away from the grain boundaries which is good for the mechanical properties. The microstructures are very similar. This is because the two compositions differ from each other marginally *i.e.* by 4% Cr.

The analysis of surface morphology and EDAX pattern from different spots reveals that the elements are distributed more or less evenly in the grain interiors and at the grain boundaries. This data should not be interpreted in the absolute sense. They can be utilized for comparison purposes, at best.

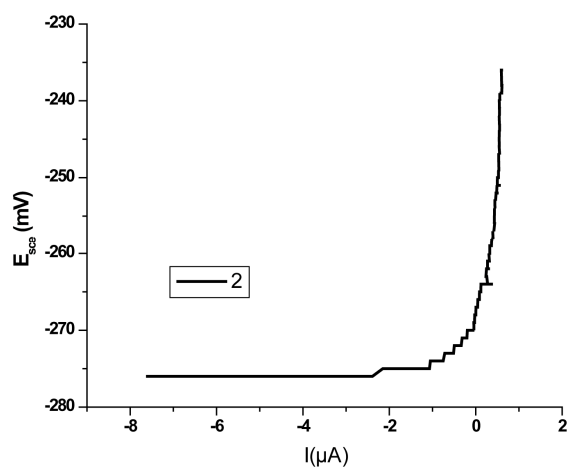
Cr and P are ferrite stabilizers. When the mixture of powders is subjected to consolidation, employing high temperature and pressure, it will undergo phase transformation. Fe powder particles would first convert to

Table 4. Corrosion data (linear polarization) for phosphoric irons in 0.5 M Na_2CO_3 + 1.0 M NaHCO_3 solution (9.4 pH).

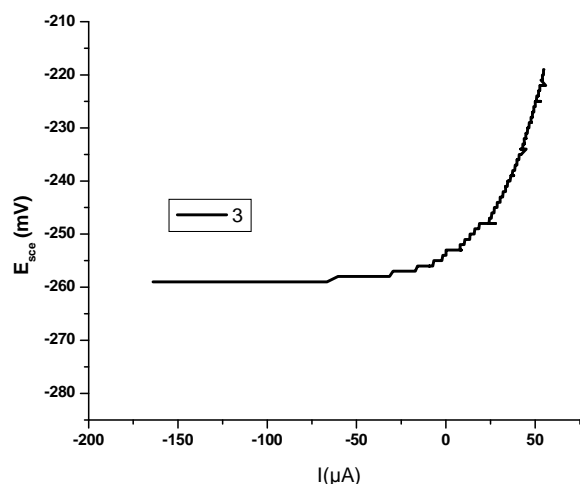
Sample	E_{corr} vs SCE (mV)	i_{corr} (μA)	Corrosion Rate (mpy)
1	-252	0.2424	0.11
2	-262.4	2.061	0.93
3	-250.8	84.85	38.28



(a)

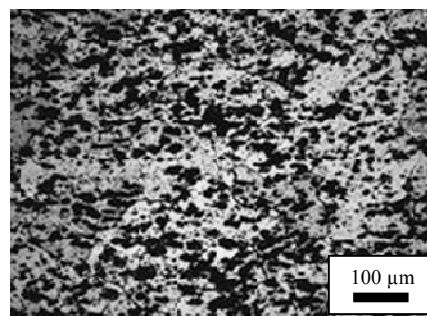


(b)

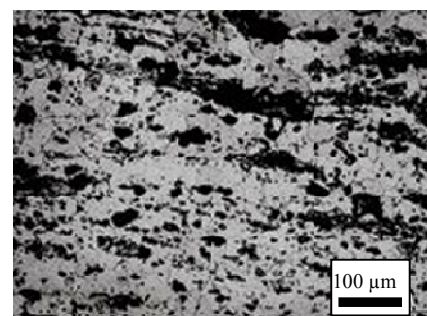


(c)

Figure 3. (a) Linear polarization curves for the sample 1 in 0.5 M Na₂CO₃ + 1.0 M NaHCO₃ solution (9.4 pH); (b) linear polarization curves for the sample 2 in 0.5 M Na₂CO₃ + 1.0 M NaHCO₃ solution (9.4 pH); (c) linear polarization curves for the sample 3 in 0.5 M Na₂CO₃ + 1.0 M NaHCO₃ solution (9.4 pH).

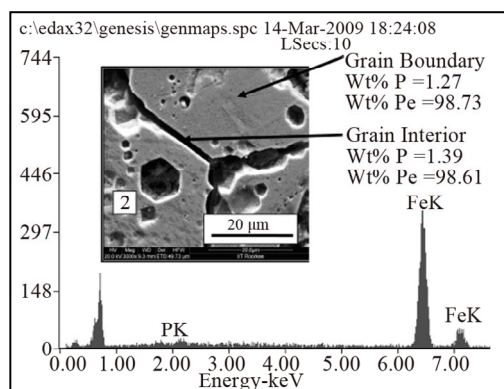


(a)

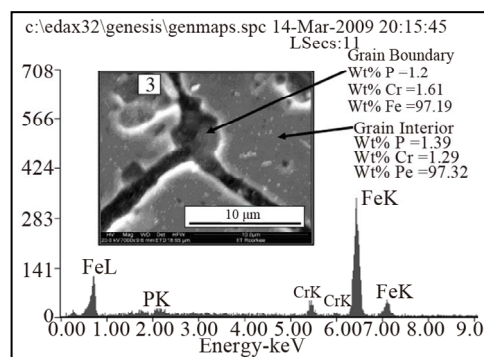


(b)

Figure 4. Microstructures of rolled and anne-a-led alloys etched with 2% Nital. Pores are elongated in the rolling direction. (a) Sample 2 & (b) Sample 3.



(a)



(b)

Figure 5. (a), (b), Surface morphology and EDAX pattern from different spots on samples 2 and 3.

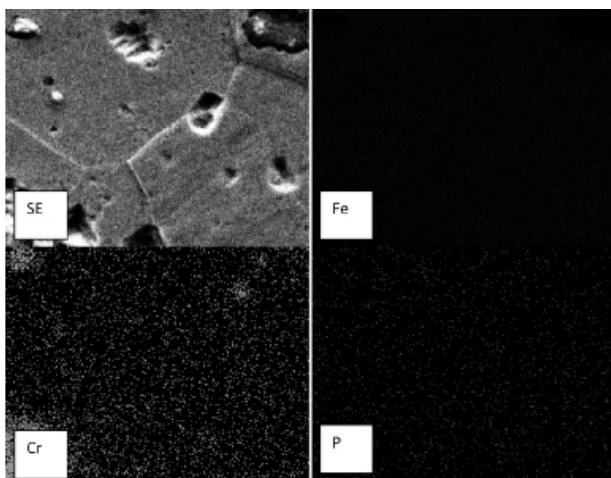


Figure 6. Composition image [secondary image] & X-ray mapping of sample 3.

gamma (FCC) iron and as ferrite stabilizers diffuse inside, they would gradually convert into alpha (BCC) iron. In this way, transfer of all the ferrite stabilizers would proceed from Fe particle surfaces towards the interior of the particles. The grain boundaries and grain interiors do not show any major differences in the concentration of P with/without chromium. Further, Briant found that the segregation of phosphorus is not affected by changes in the amounts of Ni, Cr, and Mn in the steel [20].

X-ray mapping of all the elements confirms that these elements get distributed uniformly in the entire structure showing no signs of segregation, of any alloying element.

Furthermore, both the samples had the same amount of residual porosity *i.e.* about 7 vol%. Hence they can be compared with each other.

4. Conclusions

1) Ordinarily, Powder metallurgical alloys are poor in corrosion resistance due to the inherent porosity associated with them. However, Phosphoric Irons alloyed with ferrite formers such as silicon, offer improved corrosion resistance in general, as compared with known wrought based iron systems.

2) Chromium addition in Iron-Phosphorous powder metallurgical alloys lower corrosion rates at 6.8 pH.

3) The compositions designed in this investigation are preferable under coastal/marine/de-icing salt conditions.

The second alloy can also be used under alkaline conditions.

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