Effect of chromium on the corrosion behaviour of powder-processed Fe–0.45 wt% P alloys

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Abstract. The corrosion behaviour of Fe–0.45P with/without addition of chromium, prepared by powder forging route was studied in different environments. The corrosion studies in acidic (0.25 M H₂SO₄ solution of pH 0.6) and neutral/marine (3.5% NaCl solution of pH 6.8) solutions were conducted using Tafel Extrapolation method. The rate of corrosion in alkaline medium (0.5 M Na₂CO₃ + 1.0 M NaHCO₃ solution of pH 9.4) was measured using linear polarization technique. The studies compare electrolytic Armco iron with Fe–P alloys. It was observed that, chromium improved the resistance to corrosion in acidic and marine environments. The corrosion rates were minimal in alkaline medium and low in neutral solution.

Keywords. Iron-phosphorous alloys; corrosion; powder metallurgy; forged; ancient iron.

1. Introduction

Corrosion of iron or steel is affected by exposed environment (Fontana 2006). 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 (Lorbeer & Lorenz 1980). The diffusion controlled oxygen reduction predominates in weak acid and neutral solutions. The corrosion rate is dependent on hydrogen ion concentration in case of acidic solutions (Lorbeer & Lorenz 1980).

Further, it is reported that plain carbon steel is subjected to more severe corrosion attack in a marine environment than in urban and rural media (Vera *et al* 2003). Segregation of phosphorus to grain boundaries can strongly affect intergranular stress corrosion cracking (SCC) of irons (Parkins 1990) and steels (Stencel *et al* 1987) in carbonate/bicarbonate solutions. The addition

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of Phosphorus is deleterious in its effect on alloy corrosion resistance and chromium did not affect the behaviour in de-aerated 0.1 N sulphuric acid (Cleary & Greene 1967). The addition of Chromium increased the atmospheric corrosion resistance in all the cases (Hudson & Stanners 1955).

In contrast to carbon steel, ancient iron–phosphorous alloys 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 the remarkable corrosion resistance of iron–phosphorous alloys. The presence of relatively high phosphorus 0.25 wt% in the pillar plays a major role in its excellent corrosion resistance by facilitating the formation of a protective passive film on the surface (Balasubramaniam 2000, Balasubramaniam & Ramesh Kumar 2000). Cr and Cu containing low alloy steels are suitable for application in an acidic environment while alloying steel with phosphorus is not beneficial in such an environment (Sahoo & Balasubramaniam, 2008).

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

2. Experimental

For making iron–phosphorous and iron–phosphorous–chromium alloys by powder metallurgical technique, iron powder (Fe–99.99 wt%, C–0.00 wt%; –200 mesh) was mixed with iron–phosphide (C–0.00 wt%; –200 mesh; containing 2.5 wt% P), low carbon ferro–chromium (C < 0.01 wt%; –200 mesh; containing 64% Cr).

Whereas, iron and low carbon ferro–chromium powders were of commercial purity, iron–phosphide powder was prepared by mixing iron powders with ortho–phosphoric acid. Subsequently reducing heat treatment (800°C/2 h/H₂) was given to obtain iron phosphide. The reactions are as follows:

The powder blends were manually mixed to make different alloys. About 500 g of each blended powder mixture was then poured in a mild steel capsule (as shown in figure 1).

Subsequently, the encapsulated powders were heated in a tubular furnace at 1150°C for 45 min in dry hydrogen atmosphere in order to remove the oxide layer from the surfaces of

Figure 1. Cross-section of mild steel capsule used in the present investigation.

Table 1. Composition of iron–phosphorous alloys developed in the study and Armco iron.

Sample	P(wt%)	Cr(wt%)	S(wt%)	Mn(wt%)	Al(wt%)	Ni(wt%)	Cu(wt%)	Fe
1 (Armco)	–	0.04	0.01	0.1	0.01	0.02	0.06	99.76%
2	0.45	–	–	–	–	–	–	Balance
3	0.45	3	–	–	–	–	–	Balance

the powders. Heated capsules were then forged with a 200 T capacity friction screw press to make slabs using a channel die. Two powder metallurgical alloys were made in the present investigation (table 1).

The compositions of these alloys are based on the powder mixture. Figure 2 schematically illustrates the process of making slabs by hot powder forging technique.

Figure 2. Schematic diagram illustrating the production of slab by hot forging of encapsulated powder mixture.

The slabs were then homogenized at 1200°C for 2 hours to eliminate compositional in-homogeneity. All the alloying elements are present in the form of fine particles around pure iron particles. This pure iron particle is 100% gamma-phase at the homogenizing temperature of 1200°C as per the Fe–P phase diagram proposed by Kubaschewski (1982). Phosphorous (in the form of ferro-phosphorous) combines with this gamma iron powder particle and dissolves in it. As it dissolves, it gets converted into ferrite and as ferrite phase grows out of gamma phase, more and more phosphorous penetrates in it. This helps carry chromium into the ferrite phase.

The mild steel encapsulation over the slabs was then removed by machining. The slabs, after removal of mild steel skin, were hot rolled using flat roll at ~ 900°C to make thin sheets. Rolling was carried out very slowly at ~ 900°C with 0.1 mm thickness reduction per pass. The rolling was done using small laboratory scale rolling mill with 10 cm roll diameter. The sheets were then annealed under vacuum at 950°C for 40 min to relieve the residual stresses. All the samples prepared this way were characterized in terms of density, microstructure, hardness, and tensile properties as detailed elsewhere (Trivedi *et al* 2009).

The samples (15 mm length, 15 mm width, and 2 mm thickness) for electrochemical testing were cut along the rolling direction. The surfaces were finished using SiC abrasive paper (up to 800 grit) and samples were degreased with acetone. Several samples were prepared from the starting materials for conducting reproducible experiments. One side of the samples was soldered with a copper wire. Then the soldered sample was covered with enamel exposing 1 cm² area. 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, 2006) was utilized for determining i_{corr} of the phosphoric irons and Armco electrolytic iron in 0.25 M H₂SO₄ solution of pH 0.6 and 3.5% NaCl solution 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 (ASTM Standard G102-89, 2006).

Corrosion rate in penetration units (like mils/year, mpy), was calculated from i_{corr} using the following equation (Ijsseling 1986):

$$\text{mpy} = i_{\text{corr}} \times \Lambda \times 1/\rho \times \varepsilon, \quad (3)$$

where

$$\Lambda = 128660 \text{ (equivalents.s.mil)/(Coulombs.cm.years)}$$

$$i_{\text{corr}} = \text{the corrosion current density in Amps/cm}^2 \text{ (Amp} = 1 \text{ Coulomb/s)}$$

$$\rho = \text{density (7.86 g/cm}^3 \text{, for iron)}$$

$$\varepsilon = \text{equivalent weight (27.56 g/equivalent, for iron).}$$

Linear Polarization technique was used to evaluate the corrosion rates of the iron–phosphorous alloys in 0.5 M Na₂CO₃ + 1.0 M NaHCO₃ solution of pH 9.4. A scan rate of 0.166 mV/s was used. The instantaneous corrosion rate (i_{corr}) of the specimens was obtained from the measured linear polarization resistance (LPR) using the Stern–Geary equation (Jones 1992) as follows:

$$i_{\text{corr}} = \frac{1}{2.303} \times \frac{\beta_a \beta_c}{R_p \times (\beta_a - \beta_c)} = \frac{Z}{R_p}. \quad (4)$$

In the above equation, βa = anodic Tafel slope, βc = cathodic Tafel slope, R_p = polarization resistance and, Z is a function of the Tafel slopes. The corrosion rate in mpy was calculated by using equation (3).

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 273 A 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 h 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 separately below. The cathodic reaction for the samples obtained in all the three solutions discussed above consists of a composite reaction of (Flitt & Schweinsberg 2005) hydrogen evolution

and oxygen reduction

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

3.1 Tafel extrapolation method

3.1a 0.25 M H₂SO₄ Solution (pH 0.6): The beta anodic and cathodic slopes, E_{corr} , i_{corr} and corrosion rate (mpy) obtained from the tafel curves of the samples are given in table 2 and displayed in figure 3. The E_{corr} lies between $-454 \text{ mV}_{\text{sce}}$ and $-455 \text{ mV}_{\text{sce}}$. The corrosion rate for sample 2 is 2536 mpy. The corrosion rate for sample 3 is 370 mpy and is more than that obtained for plain carbon steel (250 mpy) (Sahoo & Balasubramaniam 2008). Corrosion rate increases on increasing the concentration of H⁺ ion or decreasing the pH (Davydov *et al* 2005).

Table 2. Corrosion data (Tafel) for iron–phosphorous alloys in 0.25 M H₂SO₄ solution (0.6 pH).

Sample	Beta anodic (V/decade)	Beta cathodic (V/decade)	E_{corr} vs SCE (mV)	I _{corr} (μA)	Corrosion rate (mpy)
1	509.0E33	−181.9E − 3	−553.0	174.7	78.8
2	309.8E − 3	−394.9E − 3	−454.4	5622	2536
3	29.13E3	−113.3E − 3	−455.5	819.2	369.6

Figure 3. Tafel curves for iron–phosphorous alloys in 0.25 M H_2SO_4 solution (0.6 pH).

3.1b 3.5% NaCl Solution (pH 6.8): The Tafel plots obtained in aerated 3.5% NaCl solution are shown in figure 4. Tafel polarization curves showed diffusion controlled cathodic reaction in all cases. In this case, the diffusion-controlled oxygen reduction reaction is the dominant reaction at E_{corr} (Flitt & Schweinsberg 2005). The activation controlled anodic Tafel slopes,

Figure 4. Tafel curves for iron–phosphorous alloys in 3.5% NaCl solution (6.8 pH).

Table 3. Corrosion data (Tafel) for iron–phosphorous alloys in 3.5% NaCl solution (6.8 pH).

Sample	Beta anodic (V/decade)	E_{corr} vs SCE (mV)	I_{corr} (μA)	Corrosion rate (mpy)
1	67.08E – 3	–424.6	2.897	1.3
2	38.25E – 3	–532	5.684	2.5
3	39.06E – 3	–561.1	2.497	1.1

i_{corr} and corrosion rate (mpy) obtained from the Tafel polarization curves of samples (figure 4) are presented in table 3. Since the cathodic reaction is diffusion controlled, hence the cathodic Tafel slopes are not provided in table 3 (ASTM Standard G102-89, 2006).

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 the Tafel extrapolation method after 24 hours of immersion in unstirred, air saturated 3.5% NaCl solution (McCafferty 2005). 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 (Dexter 1979). The E_{corr} of the samples lies between $-600 \text{ mV}_{\text{SCE}}$ and $-690 \text{ mV}_{\text{SCE}}$. 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 (Sahoo & Balasubramaniam 2008).

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 1.1 to 2.5 mpy. The E_{corr} of the samples lies between $-532 \text{ mV}_{\text{SCE}}$ and $-561 \text{ mV}_{\text{SCE}}$.

3.2 Linear polarization method

3.2a 0.5 M Na_2CO_3 + 1.0 M NaHCO_3 Solution (pH 9.4): This solution was chosen to evaluate the corrosion resistance of the samples against soil (buried condition). Alkaline solutions are known to cause intergranular SCC due to segregation of phosphorous in low alloy steels (Sikora *et al* 1993).

The R_p , E_{corr} , i_{corr} and corrosion rate (mpy) obtained from the linear polarization curves of samples are provided in table 4 and displayed in figures 5a and b. The E_{corr} lies between $-250 \text{ mV}_{\text{sce}}$ and $-296 \text{ mV}_{\text{sce}}$. The corrosion rate is low and lies between 0.18–1.4 mpy (mils per year). Alloy 2 displayed lower corrosion resistance than alloy 3. Alloy 2 can be used in buried (in soil) conditions.

3.3 Segregation of alloying elements

Powder metallurgical iron–phosphorous alloys 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:

Table 4. Corrosion data (linear polarization) for iron–phosphorous alloys in 0.5 M Na_2CO_3 + 1.0 M NaHCO_3 solution (9.4 pH).

Sample	R_p Ohms	E_{corr} vs SCE (mV)	i_{corr} (μA)	Corrosion rate (mpy)
1	89600	–252	0.2424	0.11
2	52600	–250.9	0.4128	0.18
3	6903	–296.5	3.146	1.4

Figure 5a. Linear polarization curves for samples 1 and 2 in 0.5 M Na_2CO_3 + 1.0 M NaHCO_3 solution (9.4 pH).

- (i) Optical microscope (figure 6),
- (ii) Surface morphology (SEM) and EDAX pattern from different spots (figures 7, 8),
- (iii) Composition image [secondary image] and X-ray mapping (figure 9).

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

Figure 5b. Linear polarization curves for sample 3 in 0.5 M Na_2CO_3 + 1.0 M NaHCO_3 solution (9.4 pH).

Figure 6. Microstructures of rolled and annealed alloys etched with 2% Nital. Pores are elongated in the rolling direction. (a) Sample 2 and (b) sample 3.

Figure 7. Surface morphology and EDAX pattern from different spots on sample 2.

Figure 8. Surface morphology and EDAX pattern from different spots on sample 3.

actual size due to the effect of etching. The porosity and density data are given in table 5. The porosity of alloy 3 is about 4% and is slightly more than that of alloy 2 i.e. about 2%. All the grains belong to a single phase that is ferrite. No other phase can be detected.

Table 5. Calculated volume percentage of porosities of the iron–phosphorous alloys.

Sample No	As forged density (g/cc)	Rolled and annealed density (g/cc)	Theoretical density (g/cc)	Porosity in rolled and annealed wires, calculated using measured density (vol%)	Porosity in rolled and annealed wires, calculated using quantitative metallographic technique (vol%)
2	7.60	7.67	7.75	1.03	2.80
3	7.35	7.413	7.736	4.175	4.54

Figure 9. Composition image [secondary image] and X-ray mapping of sample 3.

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 3% 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.

In this respect, 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 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. Although the grain boundaries show a little higher concentration of alloying elements, the grain boundaries and grain interiors do not show any major differences in the concentration of P with/without chromium. Further, Briant (1981) found that the segregation of phosphorus is not affected by changes in the amounts of Ni, Cr, and Mn in the steel.

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, residual porosity in these samples (of the order of 2–4 vol%) has no adverse effect under moderate corrosion conditions as described above.

4. Conclusions

- (i) Ordinarily, powder metallurgical alloys are poor in corrosion resistance due to the inherent porosity associated with them. However, iron–phosphorous alloys alloyed with ferrite formers such as silicon, offer improved corrosion resistance in general, as compared with known wrought based iron systems.
- (ii) Chromium addition in iron-0.45 wt% phosphorous powder metallurgical alloys lowers the rate of corrosion in the range of pH: 0.6 to 6.8.
- (iii) The second composition designed in this investigation is preferable under alkaline conditions.
- (iv) These alloys can also be used under coastal/marine/de-icing salt conditions.

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