April, 1971] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1007—1010 (1971) 1007

Corrosion Reaction of Iron in Phosphatizing Solution

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(Received June 3, 1970)

An electrochemical investigation was made on the corrosion reaction of iron in phosphatizing solution to clarify the mechanism of the formation of phosphate coating. Polarization characteristic curves revealed the corrosion of iron to be under cathodic control implying that the formation of phosphate coating occurs thus under cathodic control. The corrosion rate increased considerably by the addition of KNO_3 or KNO_2 which is used as an accelerator in phosphatization. The formation of phosphate coating was much accelerated by cathodic polarization of iron, but repressed by anodic polarization and rotation of the iron electrode.

The rate of phosphate coating formation is believed to be controlled by the corrosion rate of metal surface phosphatized. The corrosion reaction is divided into two electrochemical reactions, anodic and cathodic.

It was suggested by Machu[1-3] that the rate of phosphate coating formation is controlled by the anodic reaction at the anodic area, occupying more than 99% of metal surface and shows first order dependency on the anodic area. However, the relation between this rate and the anodic area fails by the addition of an accelerator to the phosphatizing solution because of its depolarization effect.

We found that the phosphate coating formation is basically under cathodic control which seems quite reasonable since the corrosion reaction of metal is usually under cathodic control.

Measurement of polarization characteristic and the rate of dissolution of iron in phosphatizing solutions of various compositions were made to decide the rate-determining step and the rate of corrosion reaction. The influence of the cathodic polarization of iron in the phosphate coating formation was examined.

Experimental

Polarization Characteristic. Solutions having the compositions shown in Table 1 were prepared by dissolving guaranteed pure chemical reagents in redistilled water (electroconductivity 2.2×10^{-6} mho·cm). Because of complications that may arise due to the formation of zinc phosphate coating on iron electrode, no zinc was added to the solution.

Iron electrode, 5 mm in diameter, was cut out from a commercial mild steel whose composition is given in Table 2. The bottom was polished with 0/5 emery paper, degreased with benzene just before the measurement and the other end was inserted into a glass tube support to be rotated in the solution. The rest of the electrode surface was covered with epoxy resin for the sake of insulation from solution. The rotation speed of the iron electrode was changed from 200 to 800 rpm.

TABLE 1. COMPOSITION OF SOLUTION FOR POLARIZATION CHARACTERISTIC

H_3PO_4	KNO_3	KNO_2	pH	Atmosphere
0.23 M	0 M	0 mM	2.6	nitrogen
0.23	0	0	2.6	air
0.23	0.10	0	2.6	nitrogen
0.23	0.10	5	2.6	nitrogen

TABLE 2. COMPOSITION OF MILD STEEL USED (wt%)

C	Si	Mn	P	S	Cu	Cr	Ni
0.12	0.29	0.35	0.002	0.030	0.35	0.06	0.09

The apparatus is shown in Fig. 1. The current was recorded 30—60 sec after the application of a constant potential to the iron electrode by a potentiostat. First anodic and then cathodic polarization characteristics were measured. All the experiments were carried out at 25°C.

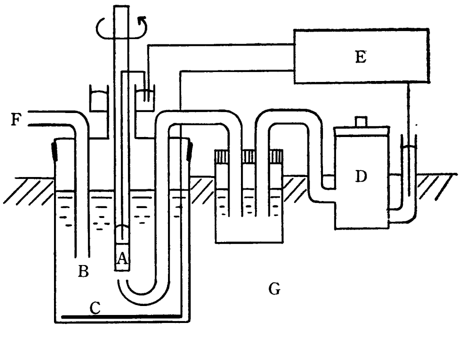

Fig. 1. Apparatus for polarization characteristic.
A: iron electrode, B: phosphatizing solution, C: Pt-electrode, D: SCE, E: potentiostat, F: N_2 or air inlet, G: thermostat

Corrosion Rate. Solutions having compositions given in Table 3 were prepared from reagent grade chemicals and distilled water. The iron electrode and cell used in the measurement of polarization characteristic were used. A polished iron electrode was dipped into the solution, rotated for a certain time and the amount of dissolved iron was determined.

TABLE 3. COMPOSITION OF SOLUTION FOR CORROSION RATE

H_3PO_4	KNO_3	KNO_2	pH	Atmosphere
0.23 M	0 M	0 mM	2.6	nitrogen
0.05—0.50	0	0	2.6	air
0.23	0.05—0.50	0	2.6	air
0.23	0	5—20	2.6	air

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[1] W. Machu, *Chem. Fabrik*, **13**, 461 (1940).

[2] W. Machu, *Korrosion u. Metallschutz*, **17**, 157 (1941); **18**, 89 (1942), **20**, 1 (1944).

[3] W, Machu, *Arch, Metallkde*, **1**, 1 (1948); **3**, 203 (1949).

Influence of Polarization on Phosphate Coating Formation. The composition of the solution is given in Table 4. The solution was prepared by dissolving ZnO in H_3PO_4 and HNO_3 and diluting with distilled water. The pH of the solution was controlled by addition of K_2CO_3.

TABLE 4. COMPOSITION OF PHOSPHATIZING SOLUTION

H_3PO_4	ZnO	HNO_3	pH
0.20 M	0.10 M	0.07 M	2.6

The same iron electrode and apparatus as those used in the experiment for polarization characteristic were used, except for the replacement of the potentiostat with a galvanostat.

A constant current was applied on the iron electrode in the phosphatizing solution and the change of iron electrode potential with time against SCE was recorded. The phosphate coating formed on the electrode was observed with a microscope.

Results and Discussion

Typical polarization characteristic curves of iron in solutions of various compositions at 600 rpm are shown in Fig. 2.

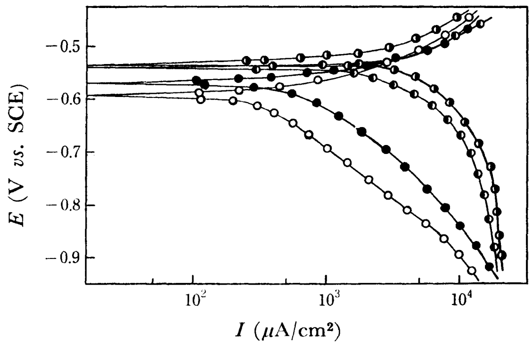

Fig. 2. Polarization characteristic of iron.
○: 0.23 M H_3PO_4 in N_2, ●: 0.23 M H_3PO_4 in air,
◐: 0.23 M H_3PO_4 + 0.10 M KNO_3 in N_2,
◑: 0.23 M H_3PO_4 + 0.10 M KNO_3 + 5 mM KNO_2 in N_2

The anodic polarization curves are smooth in all cases indicating the anodic reactions to be under diffusion control.

On the other hand, the cathodic polarization curves change appreciably with the composition of solution.

In pure H_3PO_4 under nitrogen atmosphere, a straight line called "Tafel slope" is observed on the cathodic polarization curve between the apparent current density of 500 and 5000 μA/cm² indicating the reaction to be under activation control. The intersection of extrapolated line of the Tafel slope and the corrosion potential gives an approximately 300 μA/cm² estimation of the corrosion current.

The polarization curves and the corrosion currents in this condition are not affected by the increase of rotation speed of iron electrode from 200 to 800 rpm except when current density is greater than 5000 μA/cm² where the cathodic polarization becomes slightly smaller with the increase of rotation speed. This could also be explained by the activation control of the corrosion reaction of iron.

In the air, the cathodic polarization curves are smooth for all rotation speeds throughout the range of current density. This indicates the cathodic reaction to be under diffusion control. In this case the corrosion potential becomes more noble than that under nitrogen atmosphere, as the rotation speed increases.

By addition of accelerators such as KNO_3 or KNO_2, the cathodic polarization curves show limiting currents and reactions proceed under diffusion control. The influence of dissolved oxygen is negligible in the presence of the accelerator.

It should be noted that in all cases, the polarization characteristic indicates that the corrosion reaction of iron in the phosphatizing solution namely the phosphate coating formation, is under cathodic control.

Figure 3 shows the corrosion current of iron in pure H_3PO_4 calculated from the amount of dissolved iron, assuming that the reaction is $Fe \rightarrow Fe^{2+} + 2e$, and applying the Faraday rule.

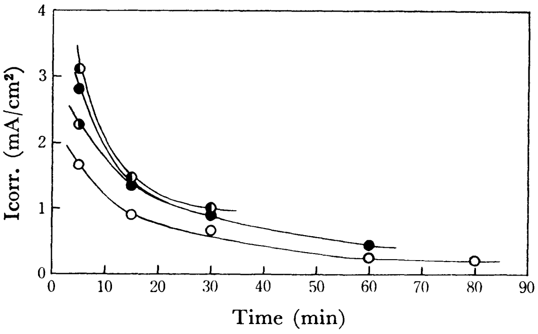

Fig. 3. Corrosion current of iron in H_3PO_4.
H_3PO_4 concn. ◐: 0.10 M Atmosphere ○: N_2
●○: 0.23 ●◐◑: air
◑: 0.50

The corrosion current diminishes exponentially with time and approaches a constant value under nitrogen or air atmosphere because of inactivation of iron surface. In the air, the corrosion rate is always greater than that under nitrogen atmosphere, while the difference of concentration of H_3PO_4 shows no influence on corrosion current. This shows that the reaction is mainly due to the oxygen dissolved in solution.

The corrosion current 300 μA/cm² obtained from the polarization characteristic corresponds to the value shown at 60—80 min in this case.

Figure 4 shows the corrosion rate of iron expressed by the dissolution rate of iron in H_3PO_4 containing various amounts of KNO_3 and KNO_2. Each plot is an average of three values obtained at 5, 15, and 30 min except those in pure H_3PO_4 which was taken only at 15 min. This is because when either KNO_3 or KNO_2 is present in the solution, the dissolved iron increases linearly with time showing constant corrosion rate within a deviation ±10%, while the corrosion rate changes considerably in the case of pure H_3PO_4. The corrosion rate increases with the increase of the concentration of added KNO_3. An increase of KNO_3 concentration from 0.05 to 0.50 M accelerates the corrosion rate by a factor of 4. KNO_2 has 30—70 times greater accelerating effect on the corrosion rate than

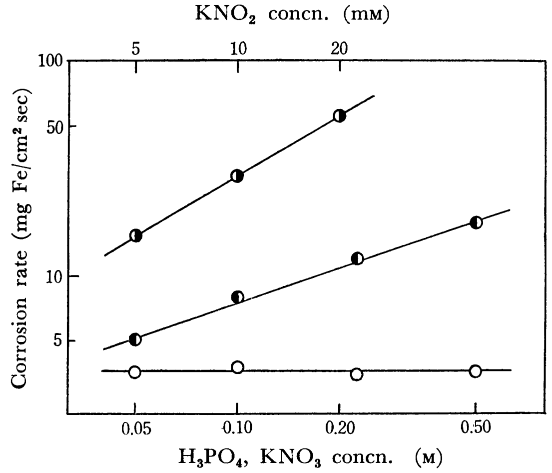

Fig. 4. Corrosion rate of iron in H_3PO_4 with KNO_3 or KNO_2.
○: pure H_3PO_4, ◐: 0.23 M H_3PO_4 + KNO_3,
◑: 0.23 M H_3PO_4+KNO_2

KNO_3.

It has also been found that the corrosion rate is not affected at all by the change of pH of the solution from 1.5 to 4.5 in pure H_3PO_4 but decreases to almost 1/6 by the same pH elevation when KNO_3 or KNO_2 is present in the solution. The increase of rotation speed of iron electrode from 100 to 600 rpm increases the corrosion rate by a factor of 2 in H_3PO_4 containing 0.1 M of KNO_3. This indicates that the corrosion rate is approximately proportional to the square root of the rotation speed of iron electrode.

When a cathodic current is applied to the iron electrode, active area on the iron surface decreases with the formation of phosphate coating, the iron electrode potential falling gradually, suddenly drops to the potential of electrodeposition of zinc. The time lap between the application of cathodic current and the sudden change of potential was measured as a phosphatizing time τ of iron electrode. Reproducibility of τ was examined and the deviation was found to be within ±20%.

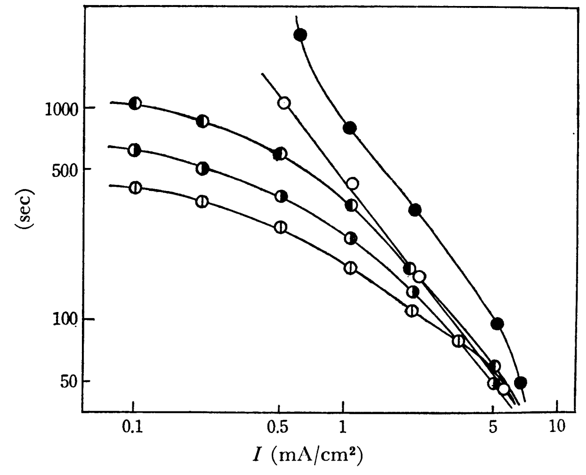

Fig. 5. Influence of cathodic polarization.
KNO$_2$ concn. ○●: 0 mM Rotation speed ○: 0 rpm
◐: 2.5 ●◐◑⦶: 600
◑: 5
⦶: 10

It is obvious from Fig. 5 that the cathodic polarization accelerates the coating formation considerably, but the rotation of electrode at 600 rpm represses it. This is due to the excessively large corrosion rate of iron surface caused by the rotation of the electrode. Coating formation is accelerated to a greater extent with the concentration of added KNO_2. The influence of cathodic polarization of iron electrode on

Fig. 6. Phosphate coating on buff-polished iron. (5 min, ×160)
Cathodic current 3 mA/cm^2, without rotation.

Fig. 7. Phosphate coating on buff-polished iron. (5 min, ×160)
Without cathodic current and rotation.

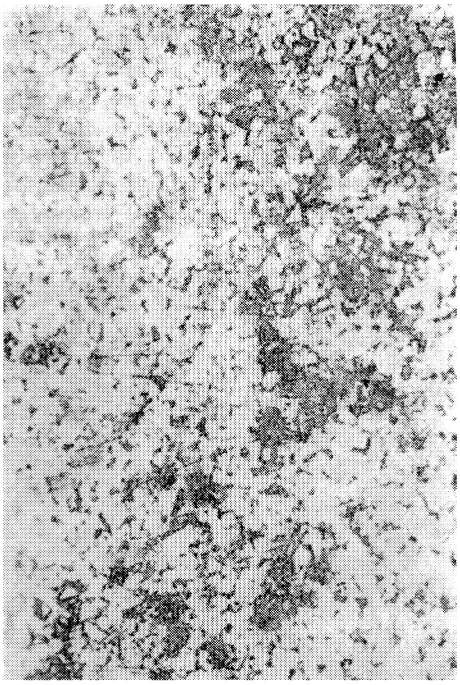

Fig. 8. Phosphate coating on buff polished iron. (5 min, ×160)
Without cathodic current, rotation at 600 rpm.

the coating formation is clearly seen in Figs. 6 and 7. This shows the phosphate coating formed on the buff-polished iron electrode.

The cathodic polarization increases the number and growth rate of phosphate crystals (Fig. 6) in comparison with that which is not polarized (Fig. 7). The rotation represses the phosphate coating and increases the corrosion of iron surface as seen in Fig. 8.

On the other hand, the anodic polarization of iron electrode shows no comparable effect on the coating formation as observed with the cathodic polarization when polarization is small. As the polarization is increased, the coating formation is repressed and the dissolution of iron electrode increases.

Conclusions

The corrosion reaction of iron which is the first step of phosphate coating formation was investigated from an electrochemical viewpoint and the following conclusions were obtained.

1) The corrosion reaction of iron in the phosphatizing solution is under cathodic control. Thus, the phosphate coating formation is also under cathodic control. The influence of diffusion rate can not be neglected.

2) The corrosion rate of iron is increased by KNO_3 and KNO_2, the latter being more effective.

3) The cathodic polarization of iron accelerates the phosphate coating formation considerably, while anodic polarization and rotation of the iron electrode represses it.