

Corrosion of pure iron in fused sodium metaphosphate

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The analytical and potentiometric study (using an Ag/Ag⁺ reference electrode) of the behaviour of pure iron in molten sodium metaphosphate at 750°C shows that a non-polarized electrode corrodes: iron is oxidized to soluble Fe²⁺ ions and, simultaneously, an Fe₂P and FeP₂ deposit resulting from phosphate anion reduction is formed on the electrode surface.

The variations of the mixed potential and of the total mass of oxidized iron show that the corrosion rate decreases as the immersion time increases. Such an inhibition comes from the gradual coating of the electrode surface with the iron phosphides: the corrosion rate is controlled by the iron diffusion through the deposit, the thickness of which increases with time.

1. Introduction

The corrosion of iron in aqueous phosphate solutions has been extensively studied. Pryor and Cohen [1] have investigated the mechanism of this corrosion in sodium orthophosphate solutions and have shown that, in deaerated solutions, iron is corroded with the formation of Fe₃(PO₄)₂ · 8 H₂O, whereas in aerated solutions iron is passivated by γ-Fe₂O₃ oxide.

The molten phosphates actually used for phosphorus, phosphoric acid or glass manufacture are fairly corrosive towards the metals and alloys employed in industrial plants.

Studies of metallic corrosion in these media have rarely been taken up. The work of Casey and Dubois [2] concerns the behaviour of nickel in molten sodium metaphosphate. No similar work seems to have been published about iron.

We were interested in the electrochemical corrosion of non-polarized pure iron in molten sodium metaphosphate at 750°C, the solution being in contact with the atmosphere.

2. Electrodes

2.1. Reference electrode

An Ag|AgPO₃, NaPO₃|NaPO₃ reference electrode is used for potential measurements. Caton [3]

has studied the reaction mechanism of this electrode.

A silver wire is dipped into a solution containing 0.4 moles of silver phosphate per kilogram of solvent (purified NaPO₃). Argon is blown through the whole device to prevent any oxidation of the silver wire.

In order to separate the (AgPO₃, NaPO₃) solution from the working electrolyte, Caton used a poorly conducting Corning n° 1720 glass membrane (the overall resistance of the electrode immersed in the melt at 700°C, measured by the author, was 3000 Ω). We improved this device by replacing (Fig. 1) this membrane by a solid α-β alumina patch welded to the lower part of a Vycor tube sheathing the electrode. α-β alumina (Al₂O₃:94.81%, Na₂O:3.59%) is an Na⁺ ionic conductor [4]. For a 10 mm thick and 6 mm in diameter patch the overall resistance of the reference electrode in the melt at 750°C is only 300 Ω.

This electrode is satisfactorily stable and reproducible: the potential difference, recorded for 6 h, between two identical electrodes is less than 15 mV. The electrode is reversible and unpolarizable: a small polarization cycle, anodic then cathodic, applied between two identical electrodes (Fig. 2) is fitted by a straight line passing through the origin.

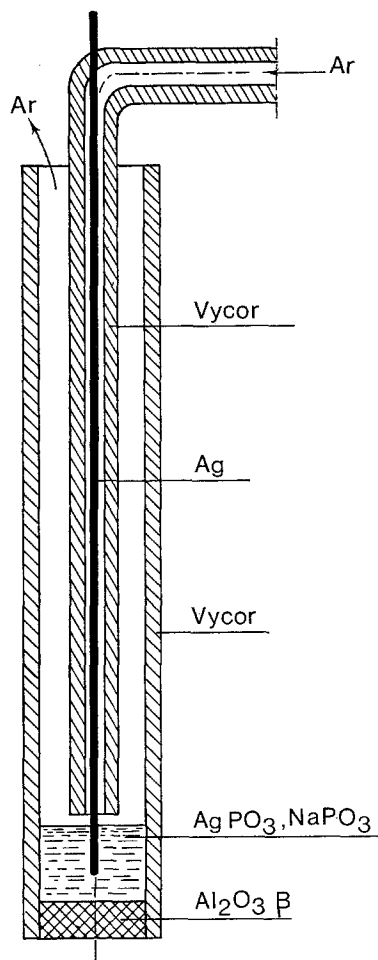


Fig. 1. Cross section of the reference electrode $\text{Ag}|\text{AgPO}_3 + \text{NaPO}_3|\text{NaPO}_3$.

2.2. Working electrode

The square shaped electrodes are cut out of a 1 mm thick Armco iron foil. The effective electrode area is 2 cm^2 . The electrode is then polished with abrasive papers having successive grain sizes of 65, 15 and $9 \mu\text{m}$. Then the shank extending from the square part of the electrode is inserted into a boron nitride casing which limits the active surface of the electrode and avoids any contact of iron with the atmosphere.

3. Solvent

3.1. Solvent constitution

The solvent was prepared according to the

method recommended by Caton [5], starting from hydrated sodium dihydrogenophosphate NaH_2PO_4 , H_2O (quality Merck analytical grade). This salt, heated in a vitreous carbon crucible at 900°C for 4 h, was on one hand partly dehydrated and on the other hand converted into sodium polyphosphate. The temperature was then lowered to 750°C .

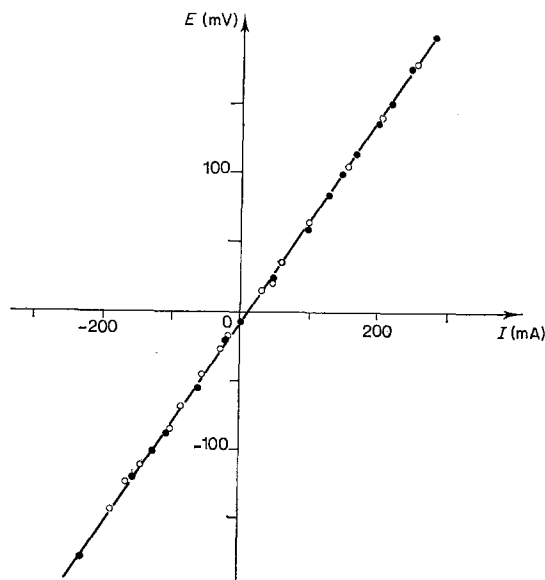
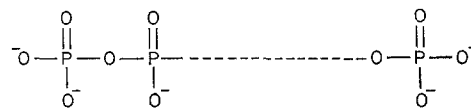


Fig. 2. The potential difference between two identical reference electrodes as a function of current. ● increasing potential difference; ○ decreasing potential difference.

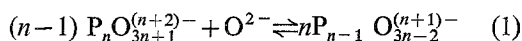
If the Na^+ ions are the only cations in the melt, the nature of the anionic composition is still questionable. It has been established [6, 7, 8], using Raman and infrared spectroscopy, that glasses obtained by rapid quenching of fused sodium metaphosphate contain mainly straight chains of polyphosphate anions. $\text{P}_n\text{O}_{3n+1}^{(n+2)-}$ according to the following diagram:



and contain few cyclic phosphate anions (metaphosphates).

It has been shown by paper chromatography [9–14] that the mean length of these chains depends on the temperature and on the partial pressure of water above the melt. The influence

of the latter parameter can be accounted for by the occurrence of acid-base equilibria such as:



Due to the experimental conditions used for the molten salt preparation, the polyphosphate anions can contain 20 to 50 phosphorus atoms [15]. Thus the solution contains very few monomer PO_4^{3-} , dimer $\text{P}_2\text{O}_7^{4-}$ or metaphosphate ions [16].

3.2. Limiting electrode processes of the solvent

3.2.1. *Experimental procedure.* The limiting electrode processes of the solvent were determined using triangular voltammetry.

Linear potential sweeps (0.5 Vs^{-1}) were applied to a vitreous carbon inert electrode having a 2 cm^2 active area. The polarization curves (Fig. 3) were recorded on a differential storage oscilloscope.

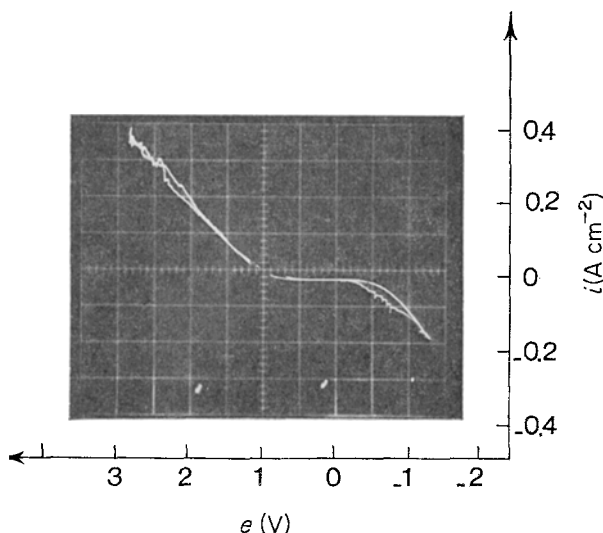
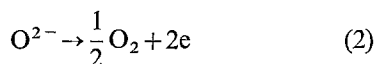
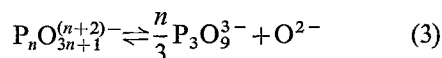


Fig. 3. Oscillogram showing the potential span between the limiting electrode reactions.

3.2.2. *Anodic reaction.* We have established that the limiting anodic reaction, starting from 0.7 V , is oxygen evolution which causes oscillations on the experimental curve (Fig. 3). The O^{2-} ions, susceptible of being oxidized according to the reaction

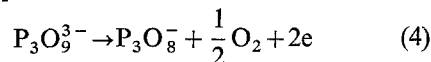


are present at a very low concentration in the solution, because of the high acidity of the melt. They can be supplied by the following equilibrium



shifting to the right and liberating $\text{P}_3\text{O}_9^{3-}$ ions.

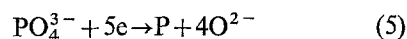
Thus, concurrently with the oxidation of the existing O^{2-} ions, the solvent oxidation reaction occurs [17]:



On the other hand, the oxidation reaction put forward by Casey and Dubois [2] seems unlikely to occur, since it involves P_3O^{2-} anions, the existence of which is doubtful.

3.2.3. *Cathodic reaction.* The limiting cathodic reaction, starting from -0.3 V , is gaseous phosphorus evolution, which causes oscillations in the polarization curve (Fig. 3).

This electrochemical reduction involves liberation of the oxide ions associated with phosphorus atoms. Equilibria such as (1) are shifted to the right. Depolymerization of the chains in the vicinity of the electrodes eventually leads to the monomer PO_4^{3-} species. So, in accordance with the scheme proposed by Franks and Inman [18], the reduction of molten sodium metaphosphate can be written:



This reduction occurs in two steps, an electrochemical one involving 2 electrons [18, 19], probably $\text{P(V)} + 2e \rightarrow \text{P(III)}$, and a chemical one consisting of disproportionation of the trivalent species $5 \text{P(III)} \rightarrow 3 \text{P(V)} + 2 \text{P(0)}$.

4. Iron corrosion

4.1. Experimental technique

An iron electrode was kept suspended in molten sodium metaphosphate without any external polarization, for time intervals increasing from 1 to 12 h, during which time the electrode potential with respect to the reference electrode was recorded.

At the end of each experiment, the iron electrode was taken out of the solution. We noticed that it was covered with a deposit and that in the vicinity of the corroded electrode, the electrolyte was colourless.

The deposits were scraped off the electrode (photomicrograph Fig. 4) and analysed by X-ray diffraction. They always consisted essentially of the iron phosphides Fe_2P and FeP_2 .

Moreover, the corrosion layer which covered the electrode was submitted to an exhaustive

Table 1. Weight percentage (wt %) of the constituent elements of the corrosion layer as a function of various immersion times of the electrode

wt %	Immersion time of the electrode in hours			
	4	6	9	12
Fe	44.72	43.11	43.84	37.93
P	28.44	29.58	28.95	33.08
Na	7.80	—	6.55	—
O ₂	20.0	—	20.5	—
H ₂ O	0	—	0	—

chemical analysis; the electrode had been previously water-washed for the soluble sodium polyphosphates to be dissolved. The constitutive elements were iron, phosphorus, oxygen and sodium. Iron was determined by atomic absorption spectrophotometry, sodium by emission spectrophotometry, oxygen and phosphorus by chemical analysis (see Table 1).

The appreciable proportions of oxygen and sodium detected showed that, in addition to iron phosphides, the corrosion layer covering the electrode contained iron phosphates and iron and sodium mixed polyphosphates. These compounds were not soluble in water and could not be eliminated during the washing operations prior to analysis.

After each experiment the entire electrolyte was analysed by atomic absorption spectrophotometry in order to determine the mass of corroded iron dissolved in the phosphate solution. The calibration curve showing the concentration of the iron ions versus the absorbance had been drawn using a pH = 1 solution containing 12 g l^{-1} sodium meta-

phosphate. Up to this concentration, the phosphates did not cause any chemical perturbation. Similarly, in order to determine the quantity of iron dissolved in the melt, the latter was dissolved in such a volume of acidified water that the sodium metaphosphate concentration was 12 g l^{-1} . The results of these analyses are presented in Table 2.

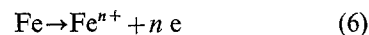
Table 2. Total mass of iron dissolved in molten sodium metaphosphate as a function of various immersion times of the electrode

Immersion time of the electrode in hours	4	6	9	12
Mass in grams of corroded iron	0.0683	0.0915	0.1318	0.1430

4.2. Corrosion reactions

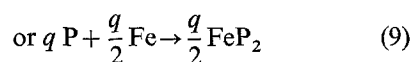
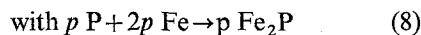
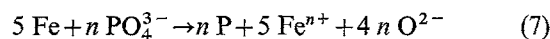
The zero-current potential of iron in sodium polyphosphate is initially -0.67 V (Fig. 5a). The potential at which the solvent is reduced according to Equation (5), equal to -0.30 V at a vitreous carbon electrode, is shifted to a more positive value at an iron electrode because of the affinity of phosphorus towards iron. Phosphide formation thus increases the potential span between the partial $e(I)$ curves for phosphate reduction (reaction (5)) and iron oxidation.

Therefore, in a wide polarization range, a mixed potential is established at the iron electrode resulting from the reduction reaction (5) and the oxidation reaction:



with $n = 2$ or 3 .

At zero current, this potential e_M is characteristic of the overall reaction:



The valency of the iron ions was determined by establishing the analytical balance of the corrosion products; a coulometric method

would yield too small a result because of the mixed working mode of the electrode. One can notice (Table 1) that the oxygen percentage depends little on the immersion time. The phosphate mass included in the corrosion layer therefore remains fairly constant. The mass of dissolved iron (Table 2) increases when the immersion time increases.

According to reactions (7), (8), (9), there is a fixed ratio $\rho = 5/n$ between the number of Fe^{n+} ions present as phosphates and the number of phosphorus atoms which are constituents of the phosphides in the deposit. ρ has been calculated from: the results of the chemical analysis of the P, O, Na elements which are constituents of the corrosion layer; and from the results of iron titrations in the solution (Tables 1 and 2).

Let the number of gram-atoms of the constituent elements of the whole corrosion layer be: a for phosphorus, b for oxygen, c for sodium and d for iron. Let e be the number of oxidized iron gram-atoms contained in the electrolyte. In order to calculate the number of phosphorus gram-atoms included in the deposit as phosphide species, we must subtract from a the amount of phosphorus gram-atoms present in the corrosion layer in the phosphate state. Since the mean value of the O/P ratio in the phosphate anions is close to 3.5 (for an equimolar $\text{PO}_3^-/\text{PO}_4^{3-}$ mixture which corresponds to a mean anion charge equal to -2), the number of phosphate gram-ions is $b/3.5$. The number of iron gram-atoms oxidized at the electrode is the sum of the iron ions present as iron phosphates in the electrolyte and in the corrosion layer. The $b/3.5$ phosphate anions present in this layer can be divided into $c/2$ sodium phosphate groups and $b/3.5 - c/2$ iron phosphate groups. The number of Fe^{n+} iron gram-ions in the iron phosphates is therefore $(b/3.5 - c/2)$.

We consequently have:

$$\rho = \frac{e + \left(\frac{b}{3.5} - \frac{c}{2}\right) \frac{2}{n}}{a - \frac{b}{3.5}} = \frac{5}{n}$$

$$\text{Hence } n = \frac{5a - 2b + c}{e}$$

Table 3 shows n values for various lengths of
Table 3. Average values of the oxidation degree of iron (n)
as a function of various immersion times of the electrode.

Immersion time of the electrode in hours	4	6	9	12
n	2.14	1.88	1.96	1.7

the immersion time of the electrode. One notices that the n values are not very different from 2. Iron is therefore oxidized to Fe^{2+} ions at the electrode, which explains why the electrolyte remained colourless in its vicinity. The oxidation reaction can thus be written

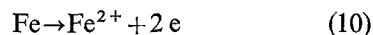


Table 3 shows an apparent decrease of the mean oxidation number of iron, which can be interpreted by phosphorus vaporization causing a phosphorus loss which becomes appreciable for long immersion times of the electrodes. Chemical analysis (Table 1) also gives the total number d of the iron gram-atoms (phosphides) and gram-ions (phosphates) contained in the corrosion layer. The number of iron gram-ions is $(b/3.5 - c/2)$ if the iron valency is 2. The μ ratio between the number of iron gram-ions and the number of phosphorus gram-atoms is

$$\mu = \frac{d - \frac{b}{3.5} + \frac{c}{2}}{a - \frac{b}{3.5}}$$

One observes (Table 4) that μ values are close

Table 4. Values of the atomic ratio $\mu = \text{Fe/P}$ as a function
of various immersion times of the electrode

Immersion time of the electrode in hours	4	6	9	12
μ	1.08	0.947	0.98	0.66

to unity, when the immersion time is between 4 and 9 h: this value of μ corresponds to the

equimolar mixture of the definite compounds $\text{Fe}_2\text{P} + \text{FeP}_2$. When the immersion time becomes long the corrosion layer grows richer in FeP_2 at the expense of Fe_2P phosphide. This result is in agreement with those of Chene [20], who found an increase in the phosphorus contents of iron phosphides prepared by prolonged electrolysis of a molten mixture of sodium metaphosphate and sodium fluoride to which ferric oxide was added.

4.3. Corrosion inhibition as a function of time

4.3.1. *Experimental results.* The values of the mixed potential of the electrode and of the total mass of oxidized iron (mass of iron ions present as phosphates) are plotted versus time respectively on curves a and b in Fig. 5. One observes that the mixed potential of the iron electrode increases as time goes on and tends, after 8 h, to become stable (about -0.480 V). The total mass of oxidized iron increases with time; the amount of iron oxidized per unit time thus decreases ($14.4 \text{ mg h}^{-1} \text{ cm}^{-2}$ after 1 h, $4.4 \text{ mg h}^{-1} \text{ cm}^{-2}$ after 8 h).

The total amount m of oxidized iron is related to the corrosion current I_{ox} by Faraday's law:

$$m = \frac{A}{nF} \int_0^t I_{\text{ox}} dt$$

We therefore have:

$$I_{\text{ox}} = \frac{nF}{A} \frac{dm}{dt}$$

The $I_{\text{ox}}(t)$ curve has been deduced from the $m(t)$ curve using the method of tangents. One observes (Fig. 5c) that the corrosion current I_{ox} decreases when the immersion time increases. There is therefore a corrosion inhibition of the non-polarized electrode. We have plotted the values of the mixed potential e_M versus I_{ox} values corresponding to various immersion times (Fig. 6).

Two iron electrodes which were immersed for 1 h (photomicrograph a, Fig. 7) and 8 h (photomicrograph b, Fig. 7) respectively, look superficially different. On photomicrograph a, the phosphide deposit, which comes out darker under the glassy phosphate layer, partly covers

the surface of the electrode, the brighter spots

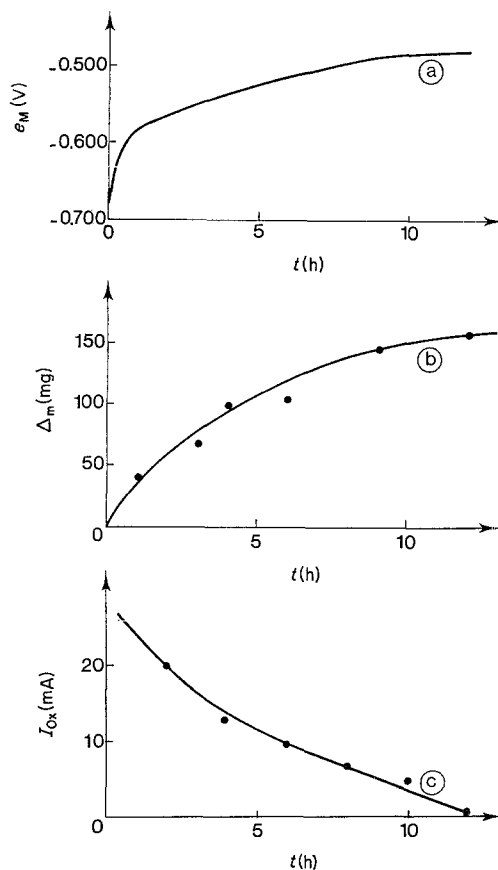


Fig. 5. a, the mixed potential at the iron electrode as a function of time; b, the total weight loss of oxidized iron as a function of time; c, the oxidation current as a function of time.

remaining uncovered. On photomicrograph b, the phosphide deposit totally covers the electrode.

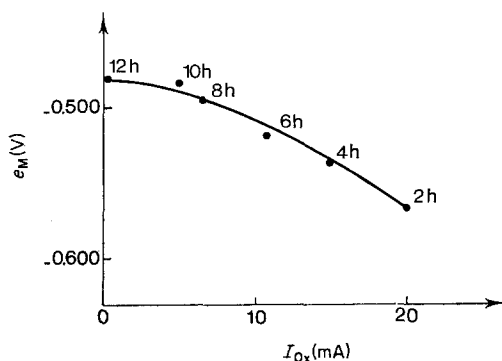


Fig. 6. The mixed potential as a function of oxidation current.

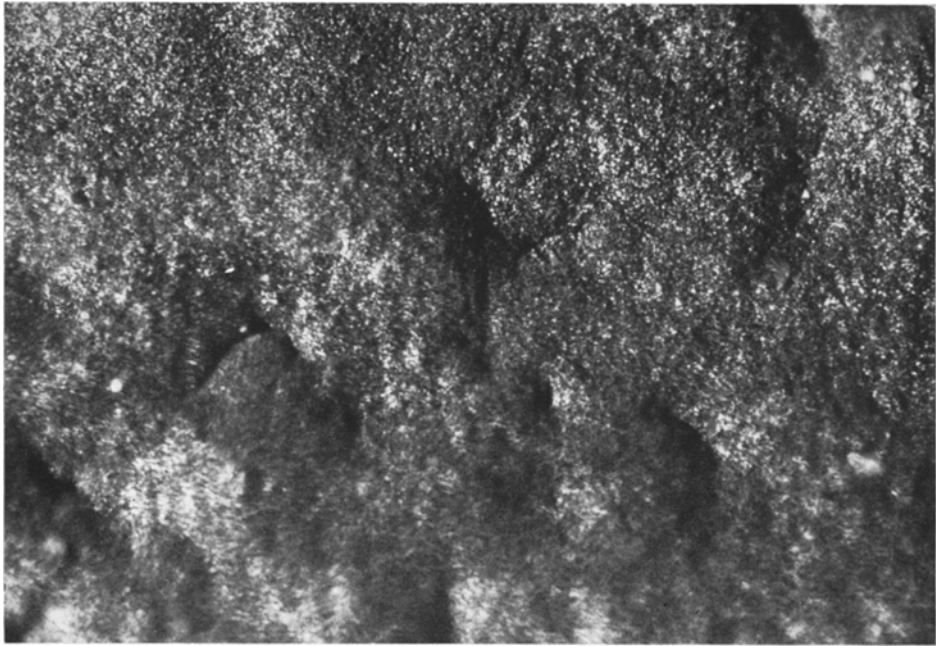


Fig. 4. Photomicrograph of the phosphides deposit detached from the electrode (magnification $\times 80$).

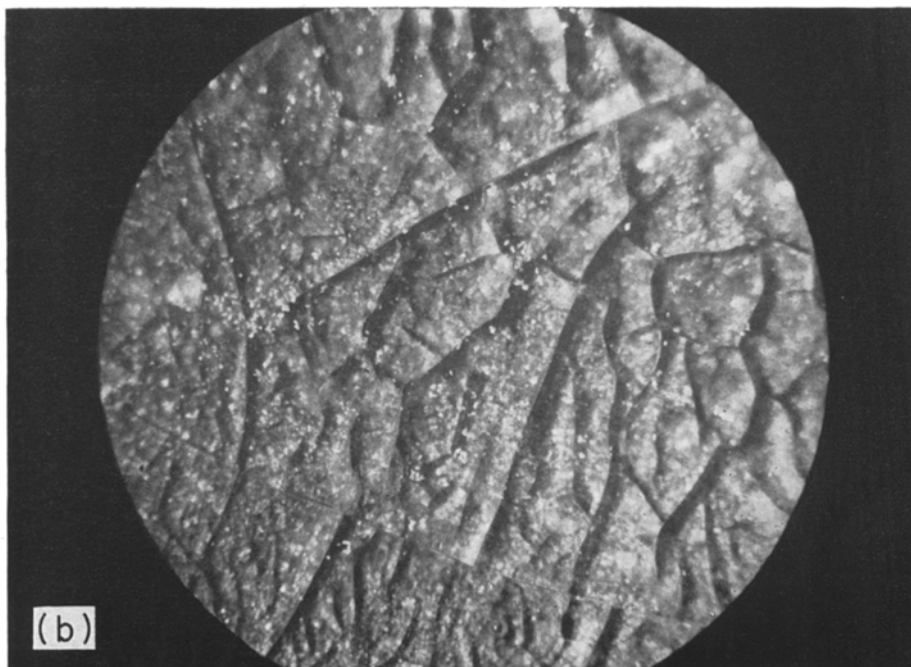
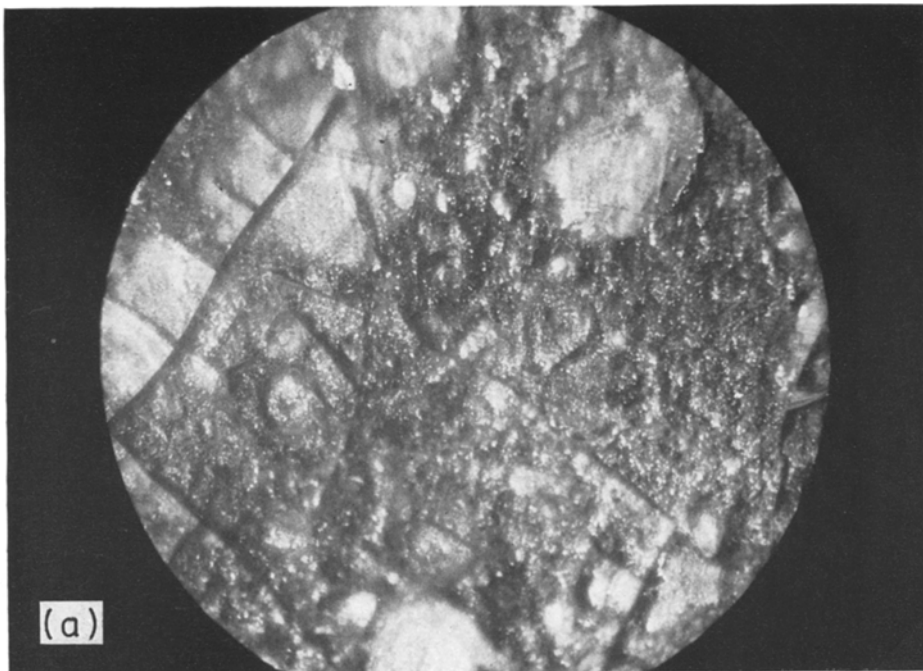


Fig. 7. Photomicrograph of the iron electrode surface. a, after 1 hour of immersion (magnification $\times 60$); b, after 8 hours of immersion (magnification $\times 60$).

4.3.2. *Discussion.* We cannot explain the increase of the mixed potential e_M with time (Figs. 5 and 6) by PO_4^{3-} anion diffusion slowing down the cathodic reaction rate, or by Fe^{2+} ions accumulation. The first mechanism would cause e_M to decrease with time and the second one would not lead to any e_M variation [21].

The observed inhibition can essentially be related, in the initial period, to the decrease of the electrode areas that are not yet covered with phosphides and are preferentially subject to oxidation. Then, when the whole electrode surface is covered, iron diffusion through the phosphide layer becomes the corrosion rate controlling factor (reaction (10)).

In fact, the reduction reaction (5) can take place at any electrode site, whether it is covered with phosphides or not, because phosphides are electronic conductors [17]. We have polarized cathodically an iron electrode in the pure sodium phosphate melt, and we have actually noticed that no passivation phenomenon appeared, although the whole electrode surface was covered by a phosphide deposit.

The oxidation reaction (10) consumes iron atoms. In the initial period, these atoms are mainly supplied by the areas that are not covered with phosphides. Calculations show that, when the anodic area decreases, the corrosion current I_{ox} decreases and the mixed potential e_M increases as observed (Figs. 5 and 6). Therefore the corrosion rate should be controlled by electrochemical transfer, which is consistent with the high value of I_{ox} observed during this period.

When the electrode surface is covered with phosphides, the iron atoms have to diffuse through the layer to be oxidized. The corrosion rate is then limited by this phenomenon and

decreases as the layer thickens. Thus the anodic reaction should be the only limiting factor; phosphorus resulting from the reduction reaction can either react with iron or the Fe_2P phosphide, or evolve in the elemental state.

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