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Corrosion behaviour of two stainless steels and a chromium cast iron in phosphoric acid contaminated with S^{2-} ions

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Various impurities such as Cl^-, F^-, SO_4^{2-} and S^{2-} contained in natural phosphates or introduced by enrichment processes, lead to many corrosion problems in equipment during the production of phosphoric acid by a wet process. Little is known about the action of S^{2-} ions in acidic media. In an attempt to investigate the mechanism of action of S^{2-} ions on stainless steels, the corrosion behaviour of three types of steel 904 L (X1NiCrMoCu25–20–5), 316 L (X2CrNiMo17–12–2) and cast iron containing 32 wt % Cr in industrial phosphoric acid contaminated with S^{2-} ions was studied, using polarization curve analysis. The characterization of the corrosion products formed on the sample surface has enabled the production of a hypothesis on the corrosion and depassivation mechanisms of steels in these media. The effect of copper and molybdenum on the corrosion resistance of the studied materials in phosphoric acid contaminated by S^{2-} ions is noted and discussed in detail.

1. Introduction

The aggressiveness of phosphoric acid produces significant corrosion problems for the equipment used in the production of phosphoric acid by a wet process. Such corrosion is not due to the phosphoric acid, which is only very slightly corrosive compared to sulfuric and hydrochloric acids. This corrosion is in fact due to impurities in the solution such as Cl^-, F^-, SO_4^{2-} and S^{2-} ions contained in the phosphate rock or from its enrichment. It is for this reason that various studies have been conducted on the influence of such impurities [1–3] and also on the choice of materials to be used [4–6]. However, to date, little work has been conducted on the corrosive effects of any sulfur impurity and thus S^{2-} ions in acidic solution [7–11]. Such a study is undertaken in the present work.

In this work, the behaviour of two stainless steels (904 L and 316 L) and also chromium cast iron in phosphoric acid contaminated by S^{2-} ions is analysed by use of polarization curves. The corrosion products formed at the sample surfaces have been characterized and an hypothesis on the corrosion and the depassivation mechanisms of the studied materials are proposed. An explanation for the greater resistance to corrosion of the 904 L stainless steel compared to the 316 L steel and chromium cast iron is also presented.

2. Experimental procedure

2.1. Materials studied

Table 1 lists the compositions of the various stainless steels used in these investigations. These materials have been selected because of their frequent use in equipment used to produce phosphoric acid.

2.2. Basic testing solution

The solution A used in this study was made from industrial phosphoric acid as described in Table II.

2.3. Equipment

Before each experiment, the working electrode was mechanically polished using abrasive paper. After several washes with distilled water, the electrode was dried and placed in the warmed (70 ± 2 °C) sample solution.

The cument–voltage curves were obtained using Amel equipment composed of a potentiostat and a logarithmic scale to measure the current, a servopilot which allows a variation of scan potential, and an X–Y plotter.

The electrochemical cell used was equipped with ground conical entry points, allowing the introduction of complementary equipment to the working electrode: the reference electrode and the counter-electrode. The reference electrode was a saturated calomel electrode ($Hg/Hg_2Cl_2/KCl$) with a potential of 250 mV/NHE. This electrode was immersed in a saturated solution of KCl at room temperature (20 °C), and was connected to the cell by an electrolytic bridge. The heating of the electrolyte was effected by distilled water circulating in the double walls that surrounded the cell connected to

TABLE I Composition of the stainless steels studied in this work

element (wt %)	C	Ni	Cr	Mo	Cu	Si	Mn
904 L	< 0.12	25	20	4–5	1.5	< 1	< 2
316 L	0.03	10–14	16–18	2–3	0	0.5	1.8
Chromium cast iron	1.6–3	0	28–32	0	0	1.5–2	0.7

TABLE II Composition (wt %) of phosphoric acid used in this work

	P_2O_5	Ca^{2+}	Mg^{2+}	Na^+	Fe^{3+}	Al^{3+}	SiO_2	SO_4^{2-}	F^-	Cl^-	Cu^{2+}
A	30.40	0.08	0.04	0.06	0.10	0.03	0.24	1.60	0.60	0.04	4ppm

the thermostated bath. The temperature, regulated by a contact thermometer was 70 ± 2 °C.

In order to reduce the experimental duration, to improve the reproducibility and to obtain more operational data, only the anodic branches of the polarization curves $I = f(E)$ were recorded. The plots were made, after a 1 h soak at the natural potential of corrosion in phosphoric acid, with a very low scan speed potential of 6mV per min.

3. Results

The plots of the current–voltage curves for the 904 L and 316 L alloys and the chromium cast iron in phosphoric acid solution "A" contaminated with S^{2-} ions are presented in Figs 1–3. An increase of the S^{2-} concentration makes the passivation of these materials quite difficult as is shown by the appearance of an activity peak in Fig. 2. This is accompanied by an increase of the passivation current density which indicates a reduction of the protective properties of the passivating layer.

The energy dispersive X-ray spectroscopy (EDS) data for the 904 L steel naturally corroded for 20 h in phosphoric acid contaminated with S^{2-} impurities is presented in Fig. 4. This analysis gives information on both the steel and the layer formed on its surface. We note the presence of sulphur, in this layer, which can only exist as a stable compound such as CuS or CdS in acidic media. The other observed elements, namely Ca, Si and Cl are from residual impurities contained in the acid.

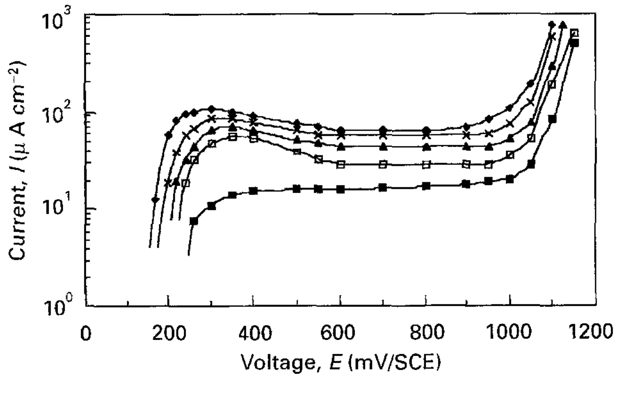

Figure 1 Curves of anodic polarization for the 904 L steel in phosphoric acid "A" solution contaminated with S^{2-} ions to the concentrations of; (■): 0, (□): 5, (△): 10, (×): 15, (◆): 20 ppm S^{2-}.

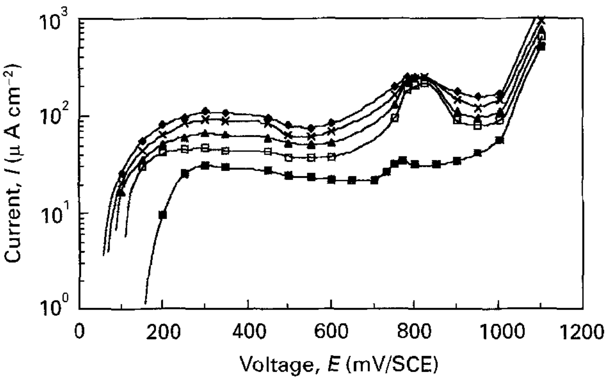

Figure 2 Curves of anodic polarization for the 316 L steel in phosphoric acid "A" solution contaminated with S^{2-} ions to the concentrations of; (■): 0, (□): 5, (△): 10, (×): 15, (◆): 20 ppm S^{2-}.

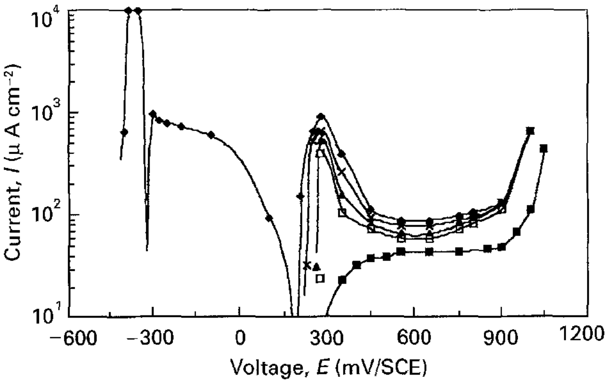

Figure 3 Curves of anodic polarization for the chromium cast iron in phosphoric acid "A" solution contaminated with S^{2-} ions to the concentrations of; (■): 0, (□): 5, (△): 10, (×): 15, (◆): 20 ppm S^{2-}.

Table III lists the main characteristic values obtained from the polarization curves for the studied materials in phosphoric acid contaminated with S^{2-} ions. We note, that an increase in the concentration of these ions, was accompanied by a decrease in the free potentials of corrosion of the 904 L and 316 L steels. In the case of the cast iron, this potential is unstable along with the critical current densities of this sample.

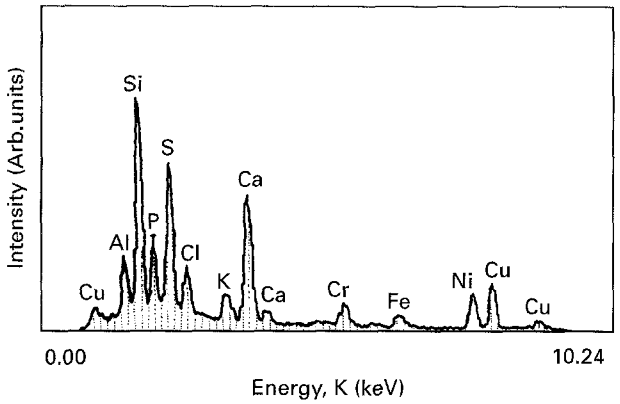

Figure 4 EDS spectrum of 904 L steel naturally corroded during 20 h in phosphoric acid contaminated with S^{2-} ions. The spectrum was obtained on the corrosion products. (Electrons accelerated at 30 kV.)

4. Discussion

The current–voltage plots obtained in these experiments generally show that the presence of S^{2-} ions in the phosphoric acid results, in a very high acceleration of the electrochemical process which results in dissolution of the metal in a low aggression media.

In phosphoric acid at about 70 °C, the addition of 5–20 ppm of S^{2-} ions leads to an increase of both the height and width of the activity peaks. As a consequence of this effect, the natural potentials of corrosion of the three alloys move to negative values. However, the 904 L steel has a good passivation behaviour, especially for concentrations of S^{2-} ions less than 10 ppm. Moreover an inverse relationship between the passivation and S^{2-} concentration was observed for this material. Indeed the depassivation potentials located at 1000, 920 and 850 mV/SCE respectively increased as the amount of S^{2-} ions decreased (5, 10, 20 ppm).

For the 316 L steel, the activity peaks are wider and the passivation fields are very narrow, in fact almost non-existent. The addition of more than 5 ppm of S^{2-} ions, leads to an increase of the transpassivity peak amplitude for a potential higher than 750 mV/SCE.

The polarization curves representing the electrochemical behaviour of chromium cast iron are different from these obtained with the 316 L and 904 L steels. Indeed, these curves show two very pronounced activity peaks, one at the low potentials of less than − 450 mV/SCE, and the other around 300 mV/SCE. The presence of these peaks shows the instability of the metal in this media. The critical current density value exceeds 10 mA cm^{-2} which reflects a strong attack on the metal.

The corrosion products produced in this attack form a protective film which restricts the dissolution of this material; this phenomenon leads to a decrease of the activity current as is shown by the current–voltage curves. For a potential exceeding 280 mV/SCE, we note the presence of a second peak with a lower density which increases according to the amount of S^{2-} added. In these conditions the width of the passivation steps decreases in consequence. However, when using industrial acid without any added S^{2-} ions, this peak does not exist and the passivation step is wider whereas the passivation current density stays high.

The metallographic observations show a uniform corrosion and the formation of a non-adherent layer on the subtrate surface. As an example, the EDS analysis of this layer by spectroscopy conducted for the 904 L steel, not only shows peaks corresponding to various impurities present in the industrial phosphoric acid used, (Al, Si, Ca, K) but also reveals peaks of sulfur and of compounds of the studied alloy (corrosion products). The sulfur can only be present in this layer in the form of metallic sulfides. We also note that the concentration of copper in this layer is higher than the concentration of any other component of the 904 L steel (Fe, Cr, Ni, Mo). This higher concentration seems to be linked to the formation of copper sulfides which are more stable in

TABLE III Influence of S^{2-} ions on the 904 L, 316 L steels and the chromium cast iron behaviour in industrial phosphoric acid at 70 °C. $E_{corr.}$: potential of corrosion expressed as mV/SCE. I_c.: critical current density expressed as μA cm^{-2}. I_p.: passivation current density expressed as μA cm^{-2}

S^{2-} (ppm)	904 L			316 L			Chromium cast iron		
	$E_{corr.}$	I_c	I_p	$E_{corr.}$	I_c	I_p	$E_{corr.}$	I_c	I_p
0	260	–	16	150	32	22	300	–	19
5	220	56	29	100	58	43	− 480 − 310 270	$> 10^4$ 600	90
10	200	71	54	70	91	72	− 480 − 310 240	$> 10^4$ 900	120
15	170	84	61	60	101	84	− 480 − 310 200	$> 10^4$ 1300	150
20	150	170	65	50	127	91	− 480 − 310 180	$> 10^4$ 1800	180

acidic media [8]. The amount of these sulfides represents around 40 wt % of the total mixture forming this layer.

Concerning the action of S^{2-} ions, there is apparently no existing model that explains the mechanism of attack of the metal by these ions in acid media. However the following mechanisms could possibly explain the action of S^{2-} ions in acid media. It is suggested that the S^{2-} ions react

(i) with H^+ ions in order to form H_2S according to the reaction:

$$S^{2-} + 2H^+ \rightarrow H_2S$$

(ii) with metallic ions present in the media, in order to form more or less stable metallic sulfides:

$$xM^{(2y/x)+} + yS^{2-} \rightarrow M_xS_y$$

(iii) by adsorption and attack of the investigated metal in order to form metallic sulfides.

$$xM + yS^{2-}_{ads} \rightarrow M_xS_y + 2ye$$

Since the pH of the media was 3.5, the metallic sulfide layer M_xS_y formed could dissolve to some extent with a resultant solution containing H_2S, HS^-, S^{2-}, and the metallic elements of soluble sulfides (Fe, Ni, Cr for example) according to the reaction:

$$M_xS_y + 2yH_3O^+ \rightarrow xM^{(2y/x)+} + yH_2S + 2yH_2O$$

$$H_2S + H_2O \rightarrow HS^- + H_3O^+$$

$$HS^- + H_2O \rightarrow S^{2-} + H_3O^+$$

With the copper being present in the media as a product of the corrosion of the stainless steel (904 L), the species H_2S, HS^- and S^{2-} are eliminated from the solution by precipitation of the sulfides Cu_2S and CuS (at pH = 3.5 we have pKs = 48 for Cu_2S and pKs = 36 for CuS).

Such an attack by S^{2-} ions naturally leads to acceleration of the anodic process for the studied alloys. It obviously depends on the passivation layer which is different according to the nature of the basic metal. It can be permeable to various ions. This may suggest that in the presence of the S^{2-} ions, some of the components of the oxidized layer could be reduced more easily than others. This causes an increase in the corrosion current density and could decrease the natural potential of corrosion as observed on the polarization curves with different concentrations of S^{2-} in the media. This anodic process, is similar for the 904 L and 316 L steels but it is different for chromium cast iron which is very sensitive to corrosion in this medium. This greater sensitivity of the latter can be explained by the nature of the metal and by the different composition of the passivation layer which is not very stable in this medium, even with the high chromium content of this alloy. This instability is shown on the anodic curve by several changes of polarity. However, this instability which disappears for 316 L and 904 L steels, may be attributed to the presence of 2 to 5 wt % of molybdenum in their composition which could lead to the production of a less porous and more protective passivation layer. This component is generally beneficial for the protection of materials, such as copper, which also has a very beneficial effect on the protective layer in acid media contaminated with S^{2-} ions. Such an effect has been assigned to a redeposition of copper in the metallic state, resulting from transformation of Cu^+ and Cu^{2+} ions. The passivation current densities recorded for the 904 L steel are lower than the ones recorded for 316 L steel which are themselves lower than the chromium cast iron ones. This underlines again the beneficial action of copper on austenitic stainless steel behaviour in this media.

5. Conclusions

From our study of the electrochemical behaviour to corrosion of 904 L, 316 L steels and chromium cast iron in industrial phosphoric acid contaminated with S^{2-} ions, at 70 °C we can draw the following conclusions;

(i) The effect of the S^{2-} ions in phosphoric acid is to increase and widen the activity peaks and to decrease the width of passivation step for the 904 L and 316 L steels while, for chromium cast iron, this passivation layer becomes unstable and even non-existent.

(ii) The presence of Mo (4 wt %) and of copper (1.5 wt %) in the 904 L steel makes it more resistant to attack by S^{2-} ions. High concentrations of Mo, strengthens the passivation layer. Moreover, copper, in the presence of S^{2-} ions, form a non-soluble barrier layer of copper sulfide at the alloy surface.

(iii) The addition of 7 ppm of S^{2-} ions to industrial acid is required to increases the passivation current density of 316 L steels. A similar behaviour has been observed for 904 L steels but at only 5 ppm of S^{2-}. For the chromium cast iron, traces of S^{2-} ions are sufficient to increase the passivation current density.

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