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Electrochemical and Analytical investigation of passive films formed on (UNS N-08028) in Simulated Phosphoric acid at different Temperature

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Abstract

The influence of temperature on the electrochemical behaviour of stainless steel was investigated in simulated and industrial phosphoric acid. Stabilisation of the passive film was studied by potentiodynamique polarisation curves, and electrochemical impedance spectroscopy (EIS) measurements. The alloy showed active-passive behaviour in this medium, an increase in temperature resulted in an increase in the passivation current density.The passive film formed on alloy sanicro 28 in simulated phosphoric acid is less stable than formed in industrial medium.

Keywords:Acid solutions, Stainless steel, EIS.

1. Introduction

Phosphoric acid in pure state is not very corrosive compared to nitric or sulphuric acids.Stainless steels have excellent corrosion resistance, resulting from thin and protective passive films, which prevent metals from reacting with corrosive environments. The influence of alloying elements on corrosion resistance is related with the stability of the passive film and its repassivation kinetics.

The aim of this research was to study the corrosion behaviour of the sanicro28, a highly-alloyed austenitic stainless steel, in simulated phosphoric acid medium polluted with sulphate and chloride ions, simulating typical industrial conditions and industrial H_3PO_4. The effect of the solution temperature on the electrochemical behaviour was evaluated by potentiodinamic curves and EIS analysis

2. Materials and methods

2.1 Materiel

The stainless steel used in this study is highly alloyed steel (UNS N-08028). Its chemical composition is given in table 1 and its commercial name that will be used all over this work is Sanicro28.

Table1: Chemical composition of study material.

Elément chimique	**C**	**Mn**	**Si**	**Cr**	**Ni**	**Mo**	**Cu**	**Fe**
Wt (%)	0,015	1,60	0,44	26,6	30,6	3,29	0,93	36,52

The cylindrical electrodes used were welded to a copper wire for the electrical contact and embedded in an epoxy resin so as to avoid crevice corrosion and leaving only an active area of 1 cm^2 in contact with the electrolyte. Prior to immersion in the electrochemical cell, electrodes were wet-ground with a series of SiC paper of decreasing grit size (120-2400), followed by rinsing with distilled water.

2.2 Solution and electrochemical cell

The electrochemical experiments were carried out in a classical three electrodes glass cell open to atmosphere and the electrolyte was not stirred. A platinum grid was used as counter electrode and saturated calomel as reference electrode (SCE). All the electrochemical measurements were performed in a simulated industrial phosphoric acid (Simulated H_3PO_4). Compositions of solutions are given in table 2. Simulated H_3PO_4 bath, pure phosphoric acid (Aldrich purity) is used with addition of chloride and sulphate with the same concentration of that industrial acid. The experiments were conducted under thermostatic conditions at 20 °C, 40 °C, 60 °C and 80 ºC in order to study the influence of temperature on the corrosion behaviour of Sanicro28.

Tableau2: Compositions of industrial H_3PO_4 and simulated H_3PO_4

Elements	Industrial H_3PO_4	Simulated H_3PO_4
P_2O_5	50 %	50%
CaO	0,50 % max	-
H_2SO_4	0,34%	0,34%
FeO_3	0,50 % max	-
Al_2O_3	1,00 % max	-
MgO	1,40 % max	-
F	0,45 % max	-
C	600 ppm max	-
Cl	0,026%	0,026%
M.S	0,1% max	-

2.3. Electrochemical tests

Open circuit potentials (OCP) were measured during 48h and electrochemical impedance spectroscopy (EIS) measurements were performed at 1h, 3h, 12h and 24h for each temperature. Impedance diagrams were obtained over a frequency range of 200 kHz to 3 mHz with ten points per decade using a 15 mV peak-to-peak sinusoidal voltage. The linearity of the system was checked in varying the amplitude of the ac signal applied to the sample. The impedance spectra were fitted using electrical equivalent circuits with Ec-Lab impedance software. Additional potentiodynamic measurements were also performed. The sample was polarizedanodically from -0.5 V/SCE to 1.5 V/SCE in the anodic direction at a scan rate of 0.5 mV/s after one hour of stabilization at OCP. In order to check the formation of pits in the passive film, potentiodynamic measurements were performed at a same scan rate of 0.5 mV/s after one hour of stabilization at OCP from OCP to 1.5 V/SCE and sweep back to 1 V/SCE. The corrosion potential (Ecorr), the transpassive potential (Etr) and the passif current density (jp) were estimated from these curves. Each experiment was performed at least three times to check reproducibility.

3. Results and discussion

3.1 Potentiodynamic tests

First, the effects of temperature on the electrochemical behaviour of the passive film of sanicro28 previously formed during 1 hour at OCP in Industrial and Simulated H_3PO_4solutionswere studied and results are reported in figures 1. Potentiodynamic curves were carried out to evaluate the electrochemical behaviour of sanicro28 in Industrial and Simulated H_3PO_4 solutions at different temperatures.

For Simulated H_3PO_4, the cathodic currents increase also with temperature and seem to be controlled by the water reduction as current increases almost exponentially with the cathodic potential. Cathodic current densities were higher than in Industrial H_3PO_4 but E_{corr} remain lower. It increases slightly from -0.214 V/SCE to -0.188 V/SCE between 20°C and 40°C, remains constant -0.188 V/SCE between 40°C and 60°C and then decrease to -0.213 V/SCE at 80°C. Ben Salah and al. [1] have observed that a polyphosphate film formed after one hour at OCP in Inustrial H_3PO_4 could explain the differences observed with simulated acid on the anodic and cathodic behaviour. Then, differences between OCP and E_{corr} are due to the reduction of the passive film in the cathodic domain. The film seems totally reduce in the Simulated acid leading to a more active surface and thus to a higher cathodic current controlled by water reduction. As soon as the potential reach the oxygen reduction domain, the rapid dissolution of the stainless steel takes place and a part of the oxygen is consumed by metallic ions to form metallic oxide as passive film. The latter strengthens progressively with the applied potential as the passive current density decreases when potential increases up to 0.5 V/SCE as observed by S. Deabate and al[2]. This trend seems to disappear at 80°C as passive current density reaches the Industrial acid curve. In this way, E_{corr} is then lower than values observed by Escivà-Cerdan [3] in anoxic conditions on Alloy31 in pure phosphoric acid contaminated by chloride, sulphate and fluorine.

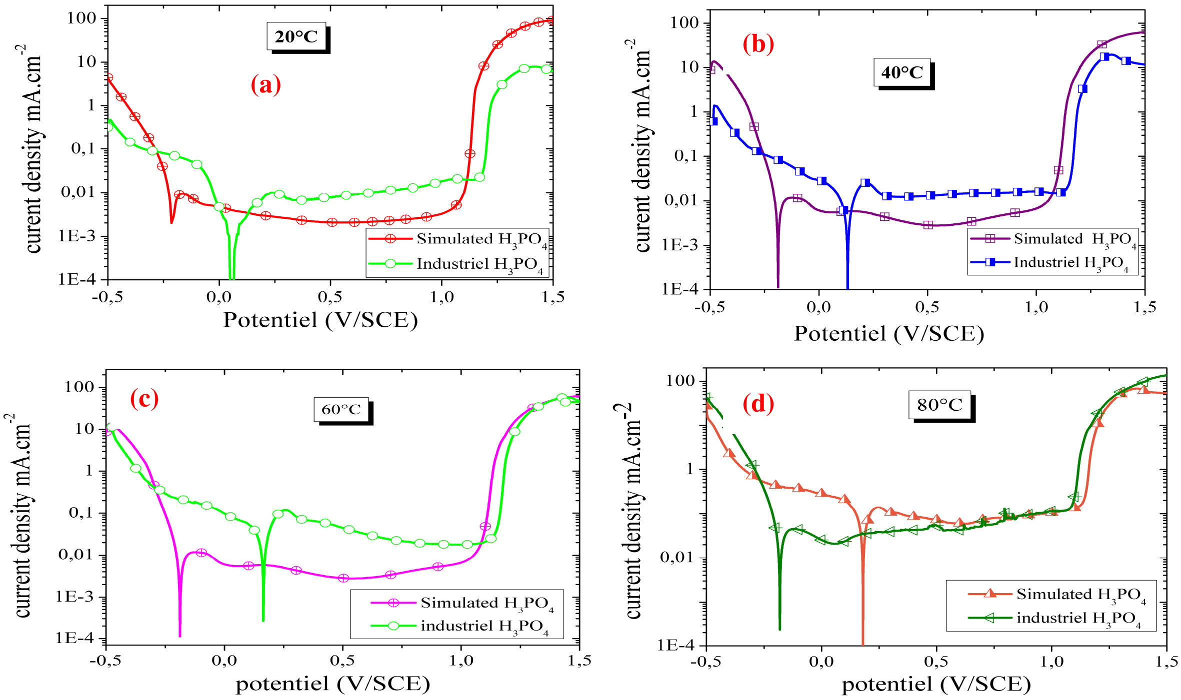

Figure1: Potentiodynamic curves of Sanicro28 SS at 20 °C (a), 40 °C (b), 60 °C (c) and 80 °C (d) obtained for Simulated and Industrial H_3PO_4 50 wt% P_2O_5.

In industrial acid, the film is also reduced, at least partially, due to the presence of the polyphosphate polymer. The water reduction current is then lower and the oxygen diffusion through the polymer controls the cathodic current leading to a current density plateau at lower cathodic potential. The polyphosphate film slows down the oxygen diffusion and the oxidation of metallic ions is delayed giving rise to more anodic E_{corr} and higher passive current densities. The values E_{corr} and i_p obtained in this solution are the same order of magnitude than [3] that seem indicated that the polyphosphate film acts as a barrier to oxygen and that the surface of the metal experiences an almost anoxic media.

For both acids, the transpassive potential decreases slightly as temperature increases but remains very high in the studied temperature range. This is due to the presence of Mo in the metal phase that enhances the stability of the passive film in chloride-containing solutions, since an insoluble protective molybdenum chloride film is formed [4]. Therefore, the transpassive potential values are not greatly influenced by the increase of the aggressiveness of chloride ions with temperature. Indeed, the difference between transpassive potential and corrosion potential, corresponding to the range of potential in which the metal was passive, decreases as temperature increases. The passivity ranges are usually higher for the materials tested in pure phosphoric acid solutions due to the fact that impurities diminish breakdown potentials (less positive values) and shift corrosion potentials to more positive values. These issues also confirm that impurities make passivation of the alloy difficult. In other words impurities somehow limit the passivation and transpassivation characteristics of sanicro 28 SS. Chloride ions cause the breakdown of the film formed on the stainless steel. Penetration through pores or defects in the film is preceded by the adsorption of anions at the film-solution interface, replacing absorbed water by adsorbed anions.

3.2 OCP measurements and electrochemical impedance analysis

The evolution versus time of OCP (figure 2) shows that OCP values of sanicro28 in simulated phosphoric acid solutions are more negative than the values registered in the Industrial medium. As previously observed by [1] the OCP values of Sanicro28 in Industrial H_3PO_4 are positive showing an ennoblement of the metal and are shifted to more positive values with increasing temperature and remain constant even at 80 °C after 48 h of immersion. This shift of OCP values was attributed to the passive nature of the studied alloy under study. During OCP tests, the passive film grows on the electrode surface, first by a selective dissolution of iron that could precipitate with phosphate as $FeHPO_4$ and $Fe_3(PO_4)_2$ [5, 6] and formation of an inner film of chromium oxide Cr_2O_3 and nickel oxide NiO [7]. It is well known that temperature promotes the diffusion of alloying elements that are involved in the formation of the passive film. The fast growth of the passive film corresponds to an ennoblement of the metal, i.e. an increase of OCP.

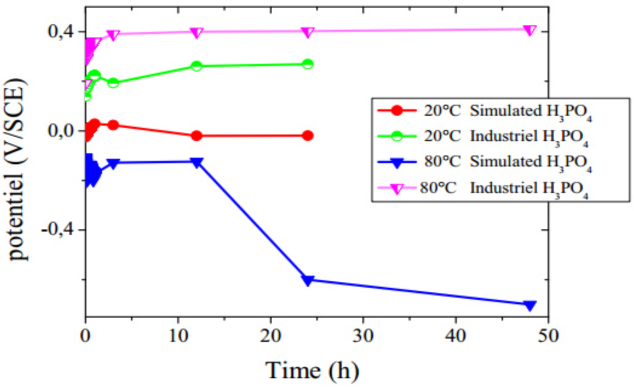

Figure 2: Open-circuit potentials versus time of Sanicro28 in industrial and simulated 50 wt. % H_3PO_4 at 20°Cand 80°C.

The evolution with time of the impedance spectra, plotted as Nyquist diagrams for each temperature is shown in figure 3. EIS were measured after 1h, 3h, 12h and 24h for immersion at 20°C, 40°C and 60°C and at 1h, 3h, 12, 24h and 48h for immersion at 80°C.Only impedances at 20 °C and 80 °C are shown. The increase in temperature increases the activity of the aggressive ions adsorbed on the surface, and consequently accelerates the dissolution process and the kinetics of exchange between the electrode surface and the electrolyte [7]. These results are confirmed by EIS measurements.

All impedance spectra present a CPE behaviour in the high frequency range characterized by an unfinished semi-circle. For Industrial acid at all temperature (figure 3a and 3b) and simulated acid at 20 °C (figure 3c), the very high values of the impedance indicate a high resistance of the metal toward corrosion characteristic of a passive film.

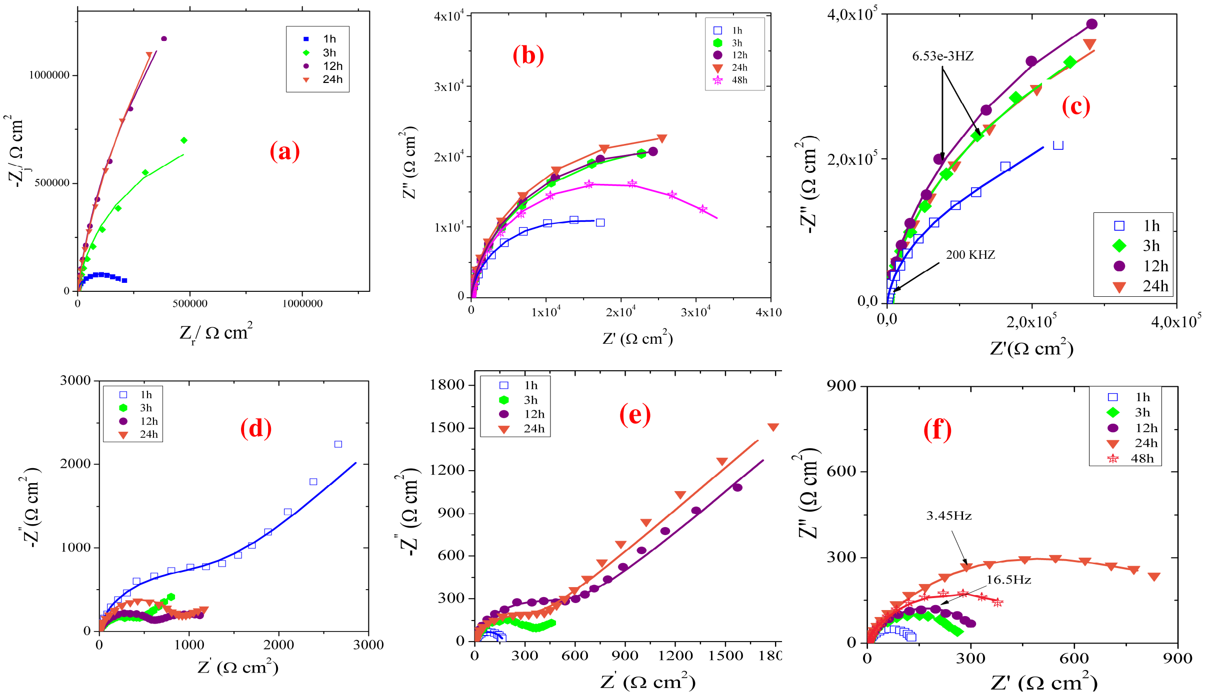

Figure3: Nyquist diagrams of Sanicro28 after 1, 3, 12, 24 h and 48h of immersion at different temperature 20 °C (a), 80° (b) in the 50 wt. % industrial H_3PO_4, 20 °C (c), 40°C (d), 60°C (e), 80 °C (f) in the 50 wt. % simulated H_3PO_4 contaminated solution with 0.34 wt. % H_2SO_4, 0.026 wt. % KCl. Straight lines correspond to fitting curves.

Impedances strongly increase with time during the first hours at OCP but remain almost constant after 12 hours of immersion in industrial acid. It takes only 3 hours to reach stability in simulated H_3PO_4. This result shows that the film stability continues to increase after 1 hour of immersion even if the OCP remains constant. The film resistance decreases as temperature increases but remains high compared to that deduced similarly from EIS measurements by Escrivà-Cerdán et al [8] on Alloy31 in polluted phosphoric acid. For Simulated acid (figure 3c to 3e), impedance measurements show, in the low frequency range, a straight line characteristic of a limiting oxygen reduction reaction due to diffusion. For Industrial acid, this diffusion is not observed due to the polyphosphate film, except at higher temperature. For Simulated acid at 20 °C (figure 3c), the oxygen diffusion is not clearly evident due to a high value of the passive film impedance. As temperture increases (figure 3d and 3e), fragilisation of the passive film give rise to a decrease in the impedance response of the passive film. Oxygen diffusion is then clearly observed in the Nyquist plots. At 80 °C, impedance of the surface decreases drastically (figure 3f) and oxygen diffusion is no more observed. At this temperature, the oxygen diffusion coefficient increase leading to oxygen reduction not limited by diffusion.

Conclusion

The electrochemical behaviour of passive film formed on alloy sanicro28 stainless steel in industrial and simulated phosphoric acid. The polarization curves revealed that the corrosion potential (E_{corr}) shifted toward more positive values, due to the enhancement of the cathodic reaction when temperature increases in simulated phosphoric acid. The passive film formed on sanicro28 at lower temperature has a superior protective ability than that formed at a higher temperature in simulated phosphoric acid.EIS measurement shows that the film is formed more rapidly in simulated media. So it is less homogenous and less resistant to chloride attack.

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