CONSIDERATION ON PITTING CORROSION OF STAINLESS STEEL

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Abstract. The pitting corrosion of 18Cc-10Ni stainless steel studied as pH function, by the electrochemical measurement applying potentiostatic technique is shown. The critical potential of pitting formation is independent of pH in acid solutions (pH range of 0.5-3.4) and it shifts to positive direction with 68 mV for pH increase by unit, in alkaline solutions (pH range of 6.9 to 12).

Key words: pitting corrosion, stainless steel, pH.

1. INTRODUCTION

The pitting corrosion of the stainless steel depends of alloy composition and structure and of physicochemical conditions of the aggressive medium. The following extern factors affect in principal the pitting corrosion: nature and concentration of the aggressive anion, the presence of the oxidants, the presence of the non-aggressive anions, the temperature and the medium pH [1-6]. The alloy may show passivity or pitting corrosion in aqueous chloride solution, depending of relative position of the open circuit potential versus of critical potential of pitting formation. The value of this potential greatly depends on metal and alloy nature, on ratio of the unaggresive anion concentration to aggressive anion concentration and pH.

This work presents the dependence of the critical potential of pitting formation of pH solutions, in the acid and alkaline range.

2. EXPERIMENTAL

The measurements were performed in a conventional three-compartment electrochemical cell separated by fretted glass disk.

In according to the presented data in the Table 1, the chloride ion concentration is practical the same, about 0.1 M, in all solutions.

The electrode assembly was made from Teflon. The working electrodes, having geometrical area of 2 cm^2, were made from 18Cr/10Ni stainless steel (18%Cr; 10%Ni; 0.04%C; 0.33%Si and Fe).

The stainless steel band was homogenised at 1050°C for one hour and water-quenched. Specimens were polished with emery paper, washed with carbon tetrachloride, followed by pickling for 5 minutes in a solution containing 15%HNO$_3$ and 2% HF (vol.) at 60°C.

A standard activation was adopted for all specimens: this consisted of cathodic polarisation at –0.8 V/SCE for five minutes. A platinum sheet with area of 4 cm^2 used as counter electrode and a saturated calomel electrode (SCE) as reference electrode.

As polarisation instrument a PAR 179 potentiostat was employed, using stepwise technique of 40 mV/ 3 minutes.

The solutions were prepared using chemically pure reagents and double distilled water. The composition and the pH values of the studied solutions are presented in the Table 1. All measurements were made at room temperature (23±1°C).

Table 1. Composition and pH of studied solutions.

Nr.	KCl, M	HCl, M	NaOH, M	pH
1	0	0.1	-	0.5
2	0.1	0.01	-	1.9
3	0.1	0.001	-	2.6
4	0.1	0.0001	-	3.4
5	0.1	-	0	6.9
6	0.1	-	0.01	9.5
7	0.1	-	0.025	11
8	0.1	-	0.050	11.5
9	0.1	-	0.075	12
10	0	-	0.075	12

3. RESULTS AND DISCUSSION

The anodic potentiostatic polarisation curves of 18Cr-10Ni stainless steel in acid solutions are presented in Fig. 1. The curves were recorded only up to the potential of

pitting formation, after that the current rapidly increases in time.

The arrows indicate the current increase in time and the corresponding potential was considered the critical potential of pitting formation. In acid solutions, in pH range of 0.5 to 3.4 the value of the pitting formation

potential is the same: –0.040 V/SCE. Figure 2 shows the anodic polarisation curves for 18Cr-10Ni obtained in the solutions of 01 M KCl in absence (curve 1) and in presence of different NaOH concentrations (curves 2-6).
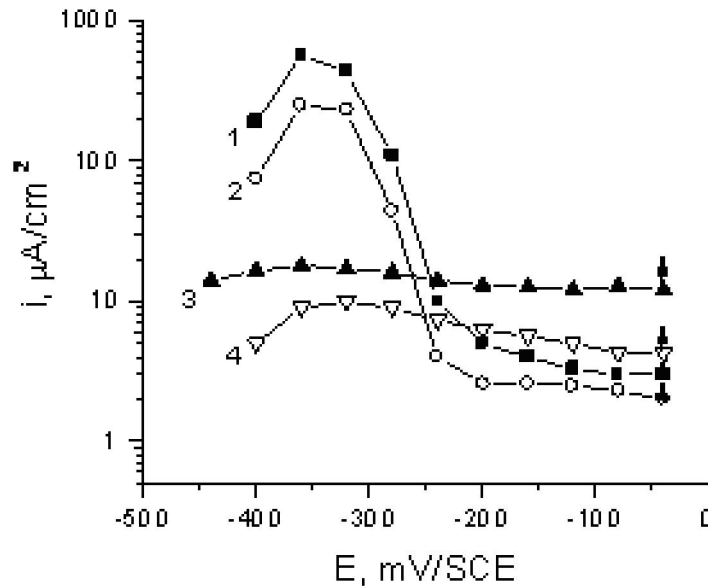

Fig. 1.Anodic potentiostatic polarisation curves (40 mV/3min.) for 18 Cr-10Ni stainless steel in acid solutions of various pH: 1 – 0.5; 2 – 1.9; 3 – 2.6; 4 – 3.4.
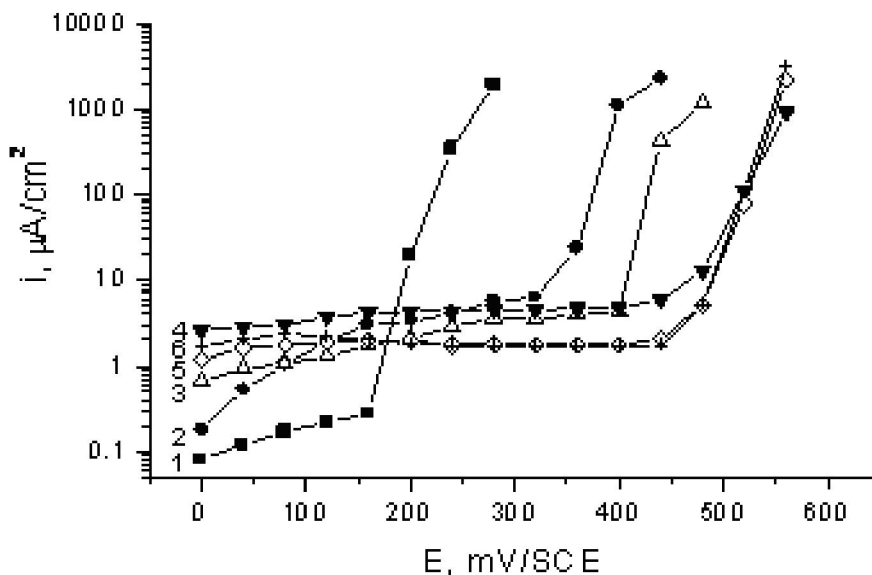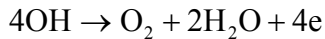

Fig. 2. Anodic potentiostatic polarisation curves for 18Cr-10Ni stainless steel in 0.1 M KCl in presence of various NaOH concentrations (M): 1 – 0; 2 – 0.01; 3 – 0.025; 4 – 0.05; 5 – 0.075; 6 – 0.075 (without KCl)

According to Fig. 2, in solutions of pH ≥7, 18Cr-10Ni stainless steel shows self-passivation, the corrosion potential is situated in the passive domain. However, in presence of chloride ion, when a certain potential is reached, pits are formed on metallic surface and the dissolution rate begins to grow rapidly (curves 1-3).

The increase of pH solution shifts the potential of pitting formation to positive direction. The dependence of the pitting potential of pH in alkaline solution is a straight line with slope of 69 mV. (Fig. 3).

Therefore, the pitting potential shifts to positive direction with pH increase., while the transpassive potential shifts to negative direction, conform to the equilibrium potentials of the possible reactions:

$$E_{e,OH/O_2} = 1.229 - 0.059pH \ [6] \ (1)$$

$$Cr + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 4e$$

$$E_{e,Cr/CrO_4^{2-}} = 0.37 - 0.079pH \ [7] \qquad (2)$$

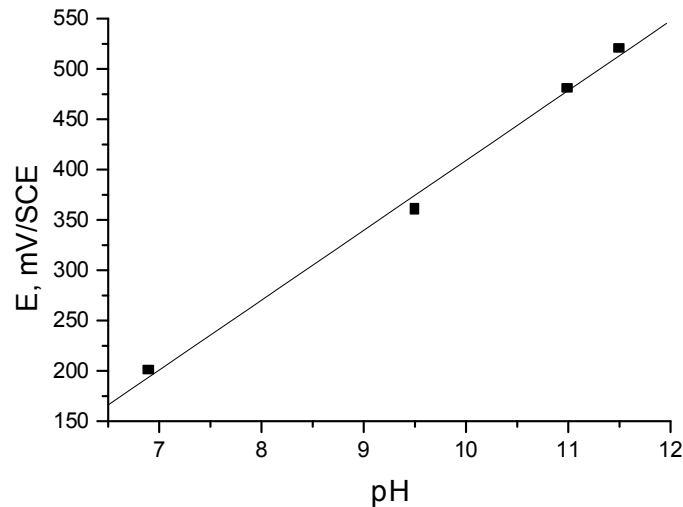$$4OH \rightarrow O_2 + 2H_2O + 4e$$

Fig.3. Pitting formation potential as pH function in alkaline solutions.

The curves 4-6 from Fig. 2 are superposed in the current increase domain. The curve 6 is obtained in the solution 10 (Table 1), which do not contain chloride ion and the current increase is due to the pass of the stainless steel in the transpassive domain. The specimen used for the curve 5, recorded in the solution 9, containing 0.075 M NaOH no pits presented after polarisation. In the solution 8, containing 0.05 M NaOH, the results are not reproducible. For very small variation of pH, the behaviour of stainless steel changes, passing from pitting corrosion to general corrosion in the transpassive domain.

CONCLUSIONS

The potential of pitting formation for 18Cr-10Ni stainless steel in acid and alkaline solutions evaluated.

In acid solutions (pH range 0.5-3.4) the potential of pitting formation is independent of pH.

In alkaline solutions (pH range 7-12) the potential of pitting formation shifts to positive direction with 68 mV/pH unit.

At pH=12, the stainless steel 18Cr/10Ni passes in the transpassive state and the pitting corrosion no place takes.

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