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STUDIES OF STEEL CORROSION IN CHLORIDE ENVIRONMENT

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ABSTRACT. The corrosion processes were studied on steel samples in different solutions, which contain Cl^- and H^+ ions.

The tests were done on a galvanostatic installation and the experimental results were used to obtain the Tafel plots. Then, the kinetic and thermodynamic parameters were calculated (the density of corrosion current, the mass index, the penetration index and the corrosion potential). Also the influence of $K_2Cr_2O_7$ addition in the corrosion environment was discussed.

KEYWORDS: corrosion sintered steel, corrosion inhibitor.

1. INTRODUCTION

Corrosion is an undesired and spontaneous process, which affects all the metallic surfaces or alloys in the presence of the corrosion agents from the environment.

The process consists in the oxidation of a metal and a reduction of one of the species from the environment.

The characteristics of this process depend on three types of factors:

a) the nature of the metal surface;
b) the nature of the corrosion agent;
c) the corrosion conditions.

The modification of one of them could produce a modification of the corrosion parameters. Thus by alloying the metallic surface the potential usually increases and passivation may occur.

For example by alloying iron with chromium, the corrosion potential increases from the value – 440 mV to + 180 mV, [9]. The final value of the corrosion potential depends of the chromium percent, [3].

This paper describes the corrosion process of a steel with low carbon content in HCl and $CaCl_2$ solutions. The chloride ion is one of the most aggressive corrosion agents and in combination with dissolved O_2 is able to form oxy-chlorides which are also soluble compounds, responsible of the corrosion, [10].

The aggressive action of the environment is reduced by adding a corrosion inhibitor as sulfate, chromate, phosphate. In this purpose we tests also the influence of $K_2 Cr_2 O_7$ on the corrosion process.

2. EXPERIMENTAL

The analyzed steel, OLC 45 is an iron alloy with the composition: 0.45 % C, 0.2%Mn, 0.17 % Si, 0.04 %S, and 0.04 % P, [4].

Tests were done on uncovered samples and samples covered with a protective chromium layer. A copper layer was first deposit on the steel sample, then the protective layer was done by galvanic covering.

Before testing, the samples were mechanically polished degreased and washed in acetone.

As corrosion agent there were used the following solutions:

HCl 0.1N
$CaCl_2$ 0.1N
HCl 0.1N +$CaCl_2$ 0.1N

The influence of $K_2Cr_2O_7$ was studied using HCl + $K_2Cr_2O_7$ solutions with concentration between 10^{-1} –10^{-3} moles/L.

Tests were done at room temperature using a galvanostatic installation, previously presented [5,6] and current-potential data were used to obtain the Tafel plots. Measurements started by evaluating the static equilibrium potential, then the intensity was stepwise modified and the potential was measured, both on the sample and on the platinum counter-electrode ($S=1cm^{2)}$) using a saturated calomel electrode as reference:

$(Hg/HgCl_2/Cl^-_{SAT}\ E_{SCE} = 0.2422\ V)$

The electrode was polarized first catodically then anodically.

3. RESULTS AND DISCUSSIONS

Using the experimental data the polarization curves were plot in the Tafel co-ordinates: lgI = F(E). (Fig. 1, and Fig. 2). Based on these plots the corrosion current I_{CORR} and potential E_{CORR} are evaluated. Same types of plots are used also for the data in the corrosion environments containing $K_2Cr_2O_7$ at different concentrations.

The corrosion potential is the thermodynamic measure of the reactivity of a metallic material in reaction with aggressive agent. This value gives information about the superficial modification of the metal which lead to a lower or a higher activity than the standard value, which is for iron: $E^0_{Fe} = -0.440$ V.

The kinetic parameters of the corrosion are: the density of the corrosion current, the corrosion rate, K_g, and the penetration index, P_{mm}.

For a sample with surface aria, A sample density of the corrosion current is given in relation (1):

$$j_{corr} = \frac{I_{corr}}{A_{sample}} \tag{1}$$

The corrosion rate, K_g and the penetration index, P_{mm} can be calculated for a metallic material with the molecular weight, M_{metal} , and the density,ρ as follows :

$$K_g = \frac{M_{metal}}{ZF} j_{corr} \ \text{[g / m}^2\text{ h]} \tag{2}$$

$$P_{mm} = \frac{K_g 8760}{\rho} \ \text{[mm / year]} \tag{3}$$

were F= 96489 A·s, is the Faraday number and Z is the number of electrons lost by the metallic material during the oxidation process.

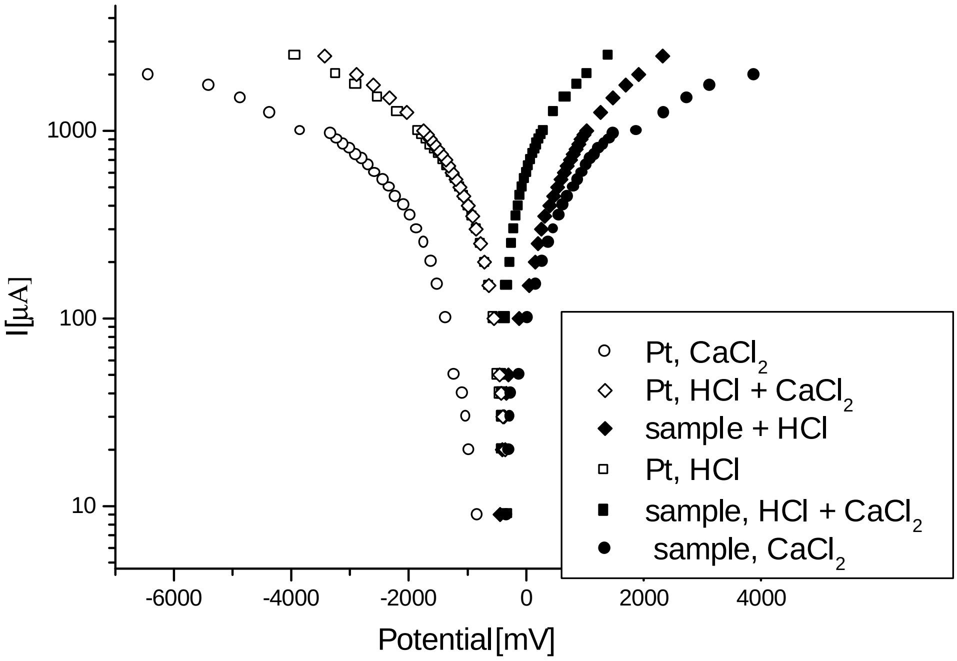

Fig. 1 Corrosion of OLC 45/Cu/Cr in different chloride solution

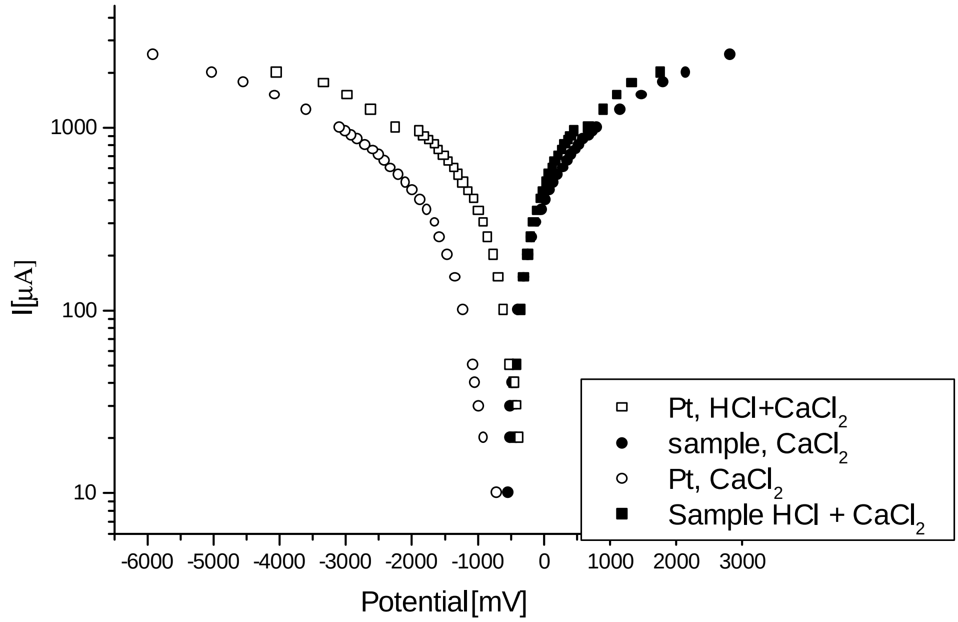

Fig. 2 Corrosion of OLC45 in different chloride solutions

Kinetic parameters

Table 1 and 2 present the kinetic parameters calculated using relations (1) –(3)

Table 1

Kinetic parameters in the absence of $K_2Cr_2O_7$:

Sample	Corrosion agent	K_g [g / m^2 h]	P_{mm} [g / m^2 h]	E_{CORR} [mV]	E_{METAL}^0 [mV]
OLC 45	HCl 0.1 n	1.68	1.87	-400	-440
OLC 45/Cu/Cr		0.91	1.1	-380	-720
OlC 45	$CaCl_2$ 0.1 n	0.38	0.42	-550	-440
OlC 45 /Cu/Cr		0.0.21	0.25	-550	-720
OlC 45	HCl + $CaCl_2$ 0.1 n	2.27	2.52	-400	-440
OlC 45/Cu/Cr		0.93	1.13	-450	-720

Table 2

Influence of adding $K_2Cr_2O_7$ on the corrosion rate of OLC45:

Sample	Corrosion agent	K_g [g / m^2 h]	P_{mm} [g / m^2 h]	E_{CORR} [mV]	E_{METAL}^0 [mV]
OLC 45	HCl 0.1 n	1.68	1.87	-400	-440
OLC 45 /Cu/Cr		0.91	1.1	-380	-720
OlC 45	HCl 0.1 n+ $K_2Cr_2O_7$ 0.1m	13.52	15.07	+120	-440
OlC 45/Cu/Cr		2.05	2.49	+515	-720
OlC 45	HCl 0.1 n + $K_2Cr_2O_7$ 0.01 m	10.56	11.56	-135	-440
OlC 45/Cu/Cr		4.37	5.31	+180	-720
OlC 45	HCl 0.1n + $K_2Cr_2O_7$ 0.001m	11.49	4.76	-125	-440
OlC 45/Cu/Cr		4.76	5.79	+125	-720

The results allow the next observations:

- For both samples the values for index penetration is:
- $(P_{mm})_{CaCl2} < (P_{mm})_{HCl} < (P_{mm})_{HCL + CaCl2}$
- A reduction of index penetration and corrosion rate for the samples covered with chromium, appears in every testing corrosion agent. So, chromium covering increases samples resistance at corrosion.
- The results obtain in $CaCl_2$ corrosion agent confirm the inhibitor action of this in a non-acid environment, [8]. In the presence of HCl and $CaCl_2$ environment the samples exhibit a cumulate effect of the chlorine ions, Cl^-, from HCl and from $CaCl_2$. Thus, the values obtain for the kinetic parameters in the presence of HCl and $CaCl_2$ environment are comparable with the values obtain by summarizing the results obtained separately in the two agents.

- Comparatively, the kinetic parameters values present a considerable increase by adding $K_2Cr_2O_7$. The chromate ions are known as anodic inhibitors, [7] but only in an non-acid environment. In a very acidic solution anodic inhibitors act like corrosion accelerators. Also, is very important to use the correct concentration of chromate: a small quantity can produce an increase of the intensity corrosion process in the already existent reaction points. The presence of the Cl^- ions may produce the pitting corrosion apparition, [2]. In this case higher quantities of inhibitor are of help only for protected samples. Fig 3 presents synthetically all theses observations.

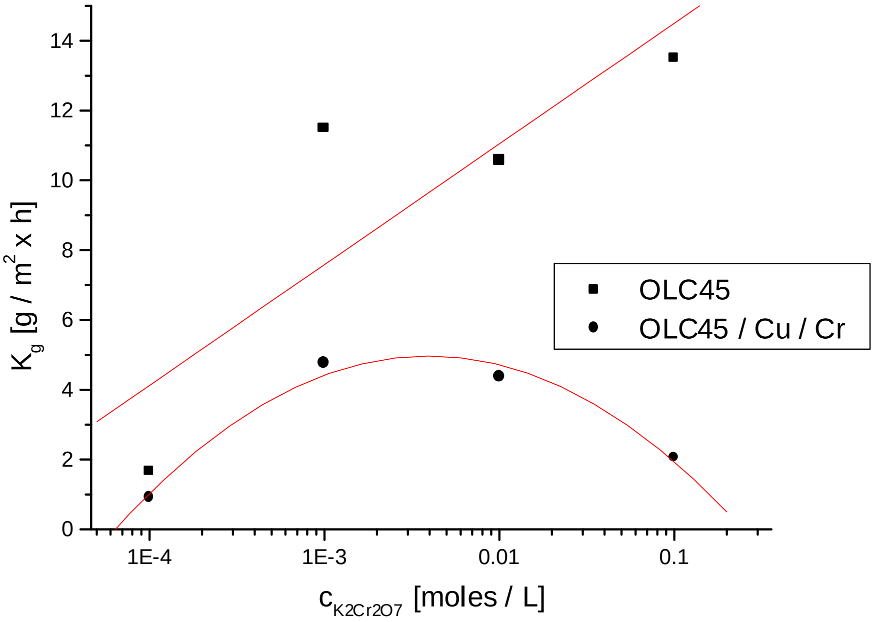

Fig. 3 Mass index of OLC 45 in HCl 0.1N + $K_2Cr_2O_7$

Thermodynamic studies

As it is know the corrosion potential value, $E_{CORR,}$ gives information about the likelihood of the processes between the metal substrate and the corrosion agent. Thus we can discussed the corrosion thermodynamic aspects.

Table 1 and table 2 give these values; In the activator absence the value of the corrosion potentials of both samples confirm the classical corrosion reaction of iron in H^+ as corrosion agent, [1]:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad (4)$$

For this reaction the electrical potential was compared with the standard value of the oxidation-reduction couple Cr^{3+} / Cr : $E^0_{Cr3+/Cr}$ = - 720 mV.

By using the activator two oxidation-reduction couples are formed: Fe^0/Fe^{2+} and Cr^{6+}/Cr^{3+}. For the last couple, the corresponding reduction equation is:

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O \qquad (5)$$

The theoretical value of the oxidation-reduction potential is [9]:

$$E^0_{Cr6+/Cr3+} = +660 \text{ mV}.$$

This value is comparable with the experimental results (Table 2).

Thus, the dominating process confirms the formation of chromium soluble compounds, responsible for the corrosion process.

4. CONCLUSION

The corrosion process was investigated in different chloride environments using a galvanostatic installation and the corrosion parameters were calculated. It was tested rough and protected steel samples with low carbon content. The steel samples protected with a copper/chromium layer have registered higher corrosion resistance than the unprotected samples due to the more inert chromium oxide layer, which increase the oxidation-reduction potential of iron, [3].

The rate of corrosion in every case was:

$(P_{mm})_{CaCl2} < (P_{mm})_{HCl} < (P_{mm})_{HCl + CaCl2}$

It was studied also the effect of adding $K_2Cr_2O_7$ in the environment.

For the uncovered samples the results confirm an activator effect of $K_2Cr_2O_7$ for the all range of the tested concentration. By covering with a chromium protective layer the corrosion resistance increases and $K_2Cr_2O_7$ may turn into an inhibitor in the higher concentrations domain.

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