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THE INFLUENCE OF WATER CONCENTRATION ON THE CORROSION OF LOW ALLOY STEELS IN THE SYSTEM METHANOL - ETHYLENE GLYCOL - FORMIC ACID

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The behaviour of three types of steel with a variable carbon content (from 0.2 to 0.4%) is studied in medium of methanol - 10% ethylene glycol - 8% formic acid with water concentration between 2% to 10%. The weight losses are measured; also the polarisation anodic and catodic curves are plotted and the corrosion parameters are established. The corrosion compounds are analysed by IR spectra, X-ray diffraction and chemical analysis. With the obtained data, a corrosion mechanism is assigned and an optimum ratio between water and acid is established in order to obtain the passive oxyhydroxylic layer.

Introduction

In the aqueous electrolytes solutions, water molecules are active participants both in the oxidation process of metals and in the passive layer formation. A lot of authors that had studied this process as Lorentz [1-4], Sato and Cohen [5], Okamoto [6-7] had shown that water molecules participate in a polinuclear structure achievement with bonds depending on the value of the anodic potential. At the value noted as the passivation potential, a partial water elimination of the film, together with a decomposition of the groups HO^- in oxygen, takes place. In nonaqueous medium, the nature and the concentration of the presented impurities play an important role [8]. These impurities determine a change of some organic medium properties such as conductivity or the dissociation constant. The main impurity in organic solvents is represented by water that has a strong influence on the equilibrium of the solution, determining changes both in the process of ions solving and in the values of the dissociation constants in the electrolyte dissociation.

This paper represents a continuation of a study which deals with water influence on corrosion of three types of low alloy steels in organic medium of ethylene glycol and/or methanol at variable water concentration, corrosion reagents being mono and dicarboxylic saturated acids [9-11]. These organic mediums represent important corrosion reagents for the ethylene glycol recuperation in installations for obtaining synthetic fibbers.

Experimental

The steel samples that are used for corrosion OL 37, OL 50 and OL 60 have the chemical composition presented in Table 1.

The steel samples of 5 cm^2 active metallic surface were cut up from a cylindrical bar. They were polished, and dyeing protected the surface that should not be corroded. The corrosion system contained methanol, 10% ethylene glycol and 8% formic acid, the water concentration varied between 2% and 10%. Karl-Fisher method was used to determine the water content. We used Merck reagents and the water was bidistilled, having electrical conductivity of 12 $\mu S\ cm^{-1}$. Also the pH-variation of the corrosion medium was measured with a HACH pH-meter.

Before introducing the sample in the corrosive system, they were submitted to a degreasing process in boiling benzene for 30 minutes and then degreased in a solution of hydrochloric acid 3% for 3 minutes. The corrosive system was open, allowing the permanent access of oxygen from the atmosphere.

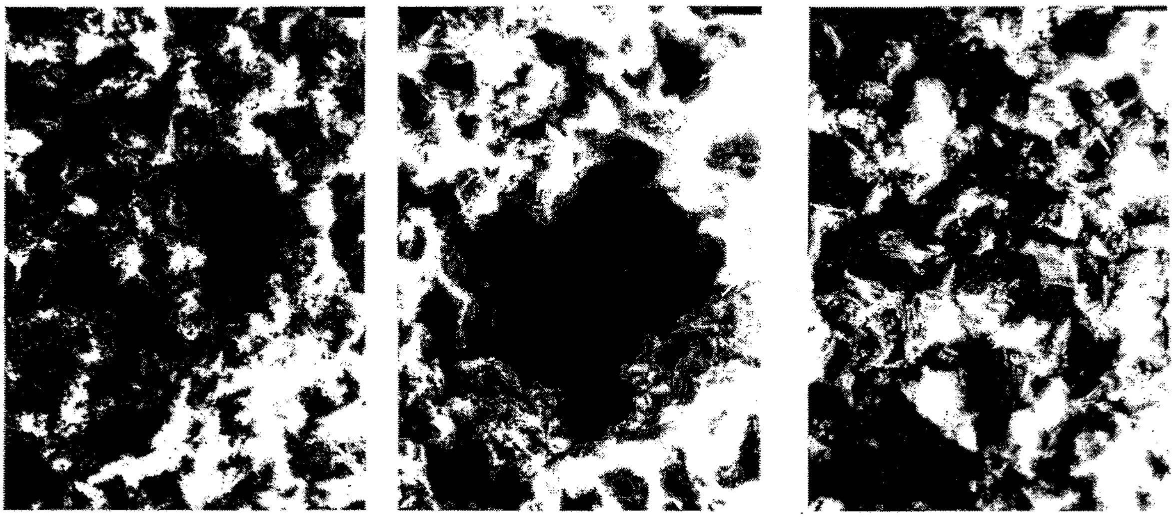
For every value of the water concentration, six metallic samples were used and were placed in the same

Table 1 The composition of steels used for corrosion

Steel	%C	%Mn	%S	%Si	%P
OL 37	0.20	0.80	0.06	0.40	0.06
OL 50	0.30	0.80	0.05	0.40	0.05
OL 60	0.40	0.80	0.05	0.40	0.05

Table 2 The values of indices K and P for the studies steels

% H_2O	OL 37 K/P	OL 50 K/P	OL 60 K/P
2	1.103/0.99	0.932/0.84	0.854/0.77
4	1.235/1.11	1.115/1.00	0.965/0.67
6	0.503/0.45	0.480/0.43	0.464/0.42
8	0.411/0.37	0.343/0.31	0.332/0.30
10	0.312/0.28	0.302/0.27	0.295//0.27



a b c

Fig.1 Aspect of the metallic surface of the steels in the system methanol - 10% ethylene glycol - 8% formic acid - 4% water (x 1200) : a-OL 37, b-OL 50, c-OL 60

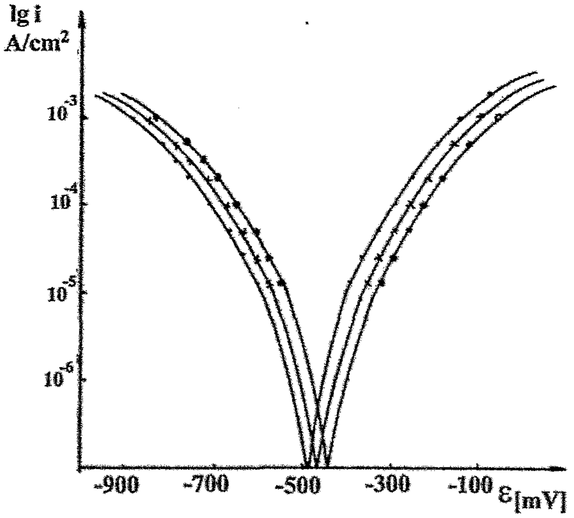


Fig.2 The polarization curves in the system methanol - 10% ethyleneglycol - 8% formic acid - 4% water : ● OL 37, x OL 50, ○ OL 60

time in the corrosive system, being subsequently taken off from 10 to 10 days, degreased with hydrochloric acid (3%) for 15 seconds and then were weighed by an analytical balance. From the values of weight losses, the gravimetric figure K (g m^{-2} h^{-1}) and the penetration P (mm m^2 $year^{-1}$) were calculated. The metallic surfaces were visualised by electron microscopy on a TESLA B300 microscope.

For the values 4%, 6% and 8% of water concentration, the catodic and anodic polarisation curves were plotted on a TACUSSEL S8R potentiometer with input impedance of 10^{12} Ω. From the shape of the polarisation curves the kinetic parameters (ε_{st}, ε_{cor} and i_{cor}) of the corrosion process were calculated.

The corrosion final compounds, for every value of water concentration, were insoluble in the system. They were analysed by X-ray diffraction on a HZG 4C Karl Zeis Yena diffractometer using Co (K_α) radiation, by IR spectroscopy on a SPECORD M82. The chemical composition (C, H, O and Fe) of the final compounds was also determined.

Results and discussion

The pH-value of the corrosion solution, at the concentration of 8% acid formic is 1.42 in an anhydrous medium. When H_2O is added to the solution, the pH-value decreases to 1.37 for 5% H_2O, fact indicating that the acid dissociation takes place in the presence of the two organic solvents, and water has no major contribution to this process.

The values of the weight losses, converted into gravimetric figure K and penetration figure P, are presented in Table 2.

Table 3 The values of the corrosion parameters in the system methanol - 10% ethyleneglycol - 8% formic acid - water

Parameters of corrosion	OL 37 % H_2O			OL 50 % H_2O			OL 60 % H_2O		
	4	6	8	4	6	8	4	6	8
ε_{st}, mV	-520	-493	-590	-475	-467	-542	-490	-448	-527
ε_{cor}, mV	-535	-510	-600	-490	-495	-555	-510	-480	-550
i_{cor}, $\mu A/cm^2$	25.36	20.36	18.87	23.86	18.12	16.35	20.12	17.25	12.78

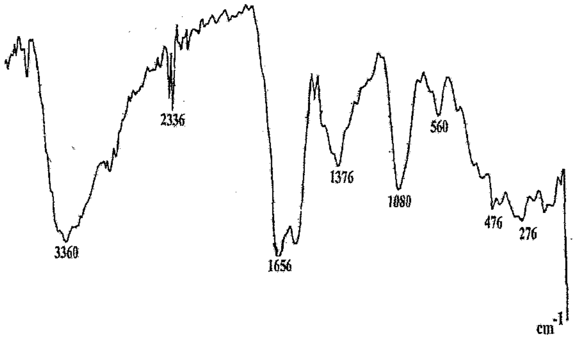


Fig.3 The IR spectrum of the corrosion compounds resulted from OL 37 in the system methanol - 10% ethyleneglycol - 8% formic acid - 4% water

Table 4 The chemical composition of the corrosion compounds in the system methanol - 10% ethyleneglycol - 8% formic acid - 4% water

%	OL 37	OL 50	OL 60
C	17.87	18.05	18.04
H	3.56	4.07	3.78
O	45.06	44.76	44.83
Fe	33.51	33.12	33.35

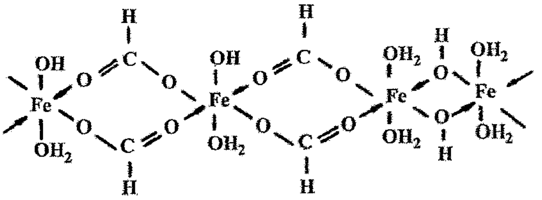


Fig.4 The structure of the corrosion compounds Fe(III) polyformiate

From these values, we can conclude that the corrosion rate is high for water concentration, higher than 4%, a fact indicating that this is the minimal percent of water necessary in passive layer formation.

The metallic surface, analysed by electron microscopy (x1200), presented a pitting corrosion for OL 37 and OL 50, and for OL 60, a generalised corrosive process with a discontinuous compound layer (Figure 1).

The polarisation curves were plotted for the values of 4%, 6% and 8% water concentration. The curves have the same variation aspect for all concentrations, not presenting passive domains in the studied potential field. The polarisation curves for 4% water concentration are presented in Figure 2. The values of the corrosion parameters calculated from these curves are presented in Table 3.

The density of the corrosion current decreases with the values of water concentration of 4% and the most stable steel in all water concentrations is OL 60.

The corrosion products are insoluble in the system at all water concentrations and do not present X-ray diffraction spectra. The IR-spectra are the same for all the systems, meaning that all the compounds presented the same absorption wave numbers. The IR absorption spectra of the corrosion compounds resulted from OL 37 in the medium containing 4% H_2O is presented in Figure 3.

The existence of two peaks, one at 276 cm^{-1} and the other at 300 cm^{-1}, characteristic of the Fe-O covalent and coordinative bonds are observed. Also the displacement of the absorption band, characteristic of the carboxyl group from the formic acid, from the value 1724 cm^{-1} to the value 1656 cm^{-1}, makes us to resume a stronger bonding of the acid [12-13]. Also, the presence of the absorption band of 1080 cm^{-1}, characteristic of the group $HO^-$from the alcohols and the peak characteristic of water are displaced at 3340 cm^{-1} respectively 2900 cm^{-1}. The rest of the peaks correspond to the vibration and rotation movements of the bonds C—C, C—H, a.s.o. [12-13].

Chemical analysis of corrosion the compounds indicates that all the products present the same composition. In Table 4, the chemical composition of the compounds obtained in the system with 4% H_2O is presented. This chemical composition is very much alike with that of a compound in which the ratio Fe/formiat radical is 1/2.

From these data, for the corrosion of iron in the system methanol-ethylene glycol-formic acid-water, the following mechanism is proposed:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2HO^-$$

$$Fe^{2+} + 2HO^- \rightarrow Fe(OH)_2$$

$$nFe(OH)_2 + 2nHCOOH \rightarrow [Fe(HCOO)_2]_n + nH_2O$$

The structure of the polymeric compound of Fe(II) with formic acid is presented in Figure 4. The hexacoordination of iron is accomplished by water molecules and ←HO— groups as bridge linkage. This structure is justified also by the little excess in the percent of oxygen and hydrogen from the elemental analysis of the corrosion compound.

Conclusion

- All three types of steel present a value for water concentration for which the corrosion rate has a maximum, and that is 4% H_2O. At the value 4% H_2O, the molar ratio water/formic acid is 1.28/1, smaller than the ratio 4/1 that is specified in literature [14-15] as being the minimum ratio in which water can participate in oxyhydroxylic layer formation. This fact can be justified by the dissociation of the formic acid and through the organic solvent molecules, the molecules of water are "free" to participate in the passive layer formation.
- The steel with the highest stability is OL 60, which has the highest carbon content. This high value of the stability may be connected to the existence in the steel's structure of a solid solution of iron-carbon, formed where the carbon concentration is over 0.3% [16].
- The corrosion mechanism is a complex one, involving dissolved oxygen. The corrosion compounds being insoluble in the organic system are submitted to a polymerisation process. These products do not form crystalline compounds.

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