

THE INFLUENCE OF WATER CONCENTRATION ON THE CORROSION OF LOW ALLOY STEELS IN THE SYSTEM METHANOL – ETHYLENE GLYCOL – ACETIC 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 - 5% acetic acid with water concentration between 1% to 5%. The weight losses are measured; also the polarisation anodic curves are plotted, and the corrosion parameters are established. IR spectroscopy, X-ray diffraction and chemical analysis are the methods used for analysing the corrosion compounds. With the obtained data, a corrosion mechanism is assigned. An optimum ratio between water and acid is established in order to obtain the passive oxyhydroxylic layer.

Introduction

In the aqueous electrolyte 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 polynuclear 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, take places. In non-aqueous 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 di-carboxylic saturated acids [9-11]. These organic mediums represent important corrosion reagents for the ethylene glycol

recuperation in installations for obtaining synthetic fibers.

Experimental part

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

The steel samples of 5 cm² 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 5% acetic acid, the water concentration varied between 1% and 5%. Karl-Fisher method was used to determine the water content. We used Merck reagents and the water was bidistilled, having electrical conductivity of 12 μS 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 time in the corrosive system, being subsequently taken

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 ₂ O	OL 37 K/P	OL 50 K/P	OL 60 K/P
1	1.115/1.00	0.983/0.88	0.773/0.69
2	1.437/1.29	1.117/1.00	0.928/0.83
3	1.654/1.39	1.228/1.10	1.118/1.01
4	1.332/1.12	0.993/0.89	0.886/0.79
5	0.816/0.73	0.719/0.64	0.627/0.56



Fig.1 a

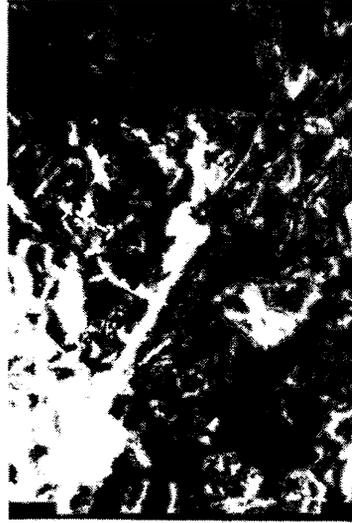


Fig.1 b



Fig.1 c

Fig.1 The metallic surface of samples in the system methanol-10% ethylene glycol-5% acetic acid-5%water (x1200). a-OL 37; b-OL 50; c-OL 60

off from 10 to 10 days, degreased with hydrochloric acid (3%) for 15 seconds and then were weighted by an analytical balance. From the values of weight losses, the gravimetric figure K ($\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) and the penetration P ($\text{mm}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$) were calculated.

The metallic surfaces were visualised by electron microscopy on a TESLA B300 microscope.

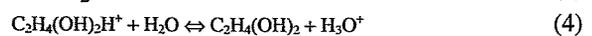
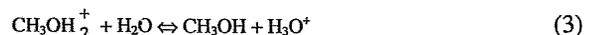
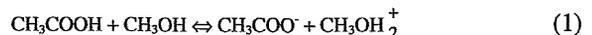
For the values 1%, 3% and 5% of water concentration, the anodic polarisation curves were plotted on a TACUSSEL S8R potentiometer with input impedance of $10^{12}\ \Omega$. From the shape of the polarisation curves the kinetic parameters (ϵ_{st} , ϵ_{cor} and i_{cor}) of the corrosion process were calculated.

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 Zeiss Jena 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 also were determined.

Results and discussion

Studying the pH -values variation, it was observed that for the anhydrous system, the pH value is 2.12 and when water is added, the pH decreases significantly till the value 2.03.

This behaviour can be justified by acid dissociation that has a maxim value in organic solvents, and when water is introduced in the system it determines a modifying of proton coordination:



The values of weight losses converted into K and P figures are presented in Table 2.

From these figures, it can be observed that the corrosion rate increases until the water concentration is 3%, than decreases.

The metallic surface, visualized by electron microscopy has the same aspect for a steel type in all the systems with variable water concentration. In Fig.1, the aspect of metallic surface, magnified by 1200 times, of all steel types in the system with 3% H₂O is presented.

For OL 37 and OL 50 it was observed that metallic surface is covered with an non-uniform layer of corrosion product and also, the obtaining of a filiform polymer compound. For OL 60 steel, the surface is also covered with a corrosion compound, but its distribution is more uniform than in other steel types.

Table 3 The values of the corrosion parameters in the system methanol - 10% ethylene glycol - acetic acid - water

Types of steels	$\epsilon_{\text{st}}, \text{mV}$			$\epsilon_{\text{cor}}, \text{mV}$			$i_{\text{cor}}, \mu\text{A}/\text{cm}^2$		
	1% H ₂ O	3% H ₂ O	5% H ₂ O	1% H ₂ O	3% H ₂ O	5% H ₂ O	1% H ₂ O	3% H ₂ O	5% H ₂ O
OL 37	-540	-550	-593	-547	-560	-600	14.18	28.26	7.94
OL 50	-520	-530	-560	-535	-542	-580	11.65	25.87	7.03
OL 60	-488	-503	-542	-510	-526	-555	9.12	23.69	6.36

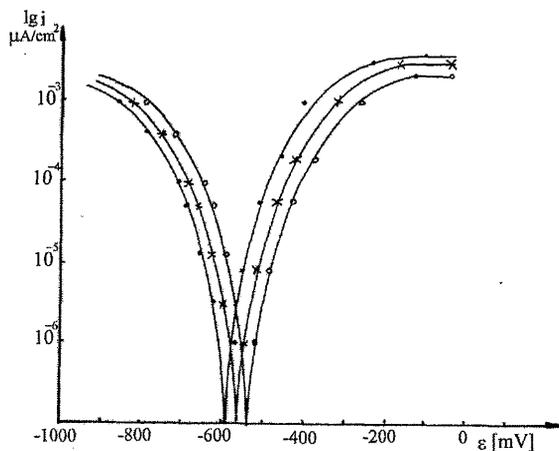


Fig.2 The polarisation curves in the system methanol-10% ethylene glycol-5% acetic acid-5%water. ●OL 37; x-OL 50;○-OL 60

The polarization curves were plotted for the values of 1%, 3% and 5% water concentration. For the values 1% and 3% water concentration, passivation was not observed. For 5% H₂O (Figure 2) a slight tendency of passivation is observed after the value -200 mV. The values of the corrosion parameters calculated from these curves are presented in Table 3.

From the data regarding the density of the corrosion current, it was observed that after 3% H₂O, the corrosion rate decreases, being in concordance with weight losses.

The corrosion final compounds from all the systems were insoluble and did not present X-ray spectra.

The I.R.-spectra are the same for all compounds derived from every steel type and in all the systems with variable water concentration, presenting peaks at the same wave numbers. In Fig.3, the IR spectrum of the corrosion compound resulted from OL 60 in the system with 5% H₂O, is presented.

The presence of two peaks at 368 cm⁻¹ and 382 cm⁻¹, characteristic for Fe-O bond, shows the two different bonding of oxygen are, a coordinative bond and a simple covalent one.

The characteristic peak of the COO⁻ group from acetic acid is displaced from the value 1718 cm⁻¹ to 1586 cm⁻¹, where a shoulder exists. This explains the coordinative and covalent bonding of oxygen from COO⁻ group, is stronger than in free acid. The presence of three peaks characteristics for HO groups from alcohols, displaced from 1080 cm⁻¹ to 1056 cm⁻¹ shows

Table 4 The chemical composition of the corrosion compounds in the system methanol - 10% ethylene glycol - 5% acetic acid - 3% water

%	OL 37	OL 50	OL 60
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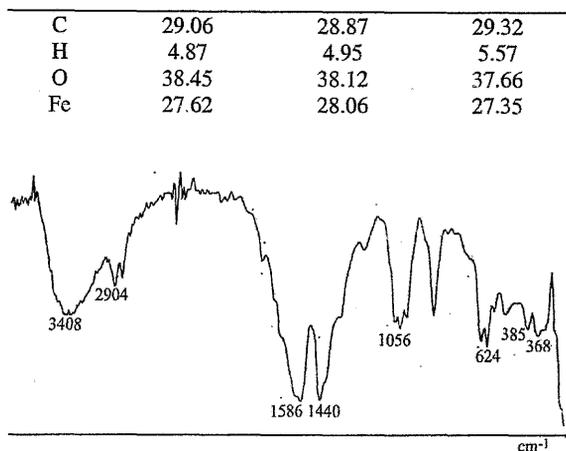


Fig.3 The IR spectrum of the corrosion compounds in the system methanol-10% ethylene glycol-5% acetic acid-5%water

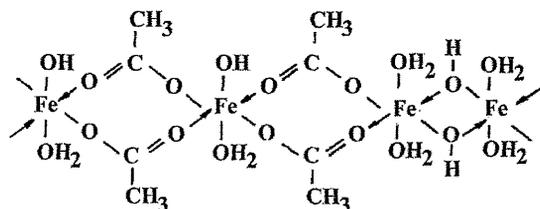


Fig.4 The structure of the Fe(III) poliacetate

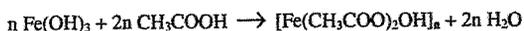
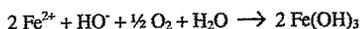
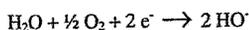
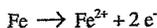
that oxygen from this group participates to stronger bonding with heavier atoms, for instance iron [12-13].

Also, the presence of a double peak around the value of 2800 cm⁻¹, shows that HO⁻ groups from water participate in bridge linkage ←OH— [12].

The chemical elemental composition of the corrosion compounds is also similar for the different steel types and systems with variable water concentration. In Table 4, the chemical composition of the corrosion compounds from the system with 5% H₂O is presented.

From these data, the ratio between iron and acetate radical from the corrosion compounds is 1/2 with a little deficiency in iron.

From the presented observations, the following corrosion mechanism is proposed:



The structure of this polymeric acetate is presented in Fig.4.

The hexacoordination of iron and the final chain molecules are accomplished by water molecules or by oxygen coordination from organic solvents.

Conclusion

- The molar ratio water/acid, where water can participate in oxyhydroxylic passive layer formation is 2/1, is smaller than the ratio indicated by literature [14-15]. The smaller value of this ratio is due to the proton coordination (proton resulted from the acid) to the organic solvents molecules, fact that determines a decreasing of water quantity necessary for the protective layer formation.
- The steel having 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 that involves the dissolved oxygen.

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