

## THE INFLUENCE OF WATER CONCENTRATION ON THE CORROSION OF LOW ALLOY STEELS IN THE SYSTEM METHANOL – ETHYLENE GLYCOL – MALONIC ACID

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The behaviour of three type of steel, with a variable carbon concentration (from 0.20 to 0.40 %) is studied in medium of methanol – 10 % ethylene glycol – 5 % malonic acid with water concentration varying between 1 % to 5 %. The weight losses are measured; also the polarisation curves are plotted and the corrosion parameters are established. SEM visualized the metallic surface. The corrosion compounds are analysed by IR spectroscopy, X-ray diffraction and chemical analysis.

**Keywords:** steel corrosion

### Introduction

In organic medium, in which water is present as impurity, the corrosion mechanisms of metals, in general, are different than those that occurs in aqueous solutions. In non-aqueous media the formation of oxyhydroxylic layer does not use the HO<sup>-</sup> groups derived from water as it happens in aqueous solutions [1-4]. This is possible only if the number of water moles is higher than the corrosive acid, meaning the ratio water/acid being higher than 4/1 [5-6]. It is known that the H<sup>+</sup> ion co-ordinates 4 water molecules. Also, some other impurities contained in organic media presented a much higher influence over the corrosion process than their presence in aqueous solutions. Their influence is shown in changings that appear in the conductivity values and also in the dissociation constant [7-8].

This paper continues the study about the influence of water concentration over steels with different carbon concentration. The steels have the composition situated at the limit between cementite and Fe-C solution. The corrosion reagents are organic acids and the medium in methanol with 10 % ethylene glycol [9-13]. In this paper, malonic acid is the corrosive reagent.

### Experimental

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

The steel samples of 5 cm<sup>2</sup> 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, 5 % malonic acid, HOOC-CH<sub>2</sub>-COOH and 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 bi-distilled, having electrical conductivity of 12 μS cm<sup>-1</sup>. Also the pH-variation of the corrosion medium was measured with a HACH pH-meter.

Before introducing the samples 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 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<sup>-2</sup> h<sup>-1</sup>) and the penetration figure P (mm m<sup>2</sup> year<sup>-1</sup>) were calculated.

The metallic surfaces were visualized by electron microscopy of a TESLA B300 microscope.

For the value of 5 % of water concentration, the polarization curves were plotted on a Digital Electrochemical Analyser DEA 332, made by RADIOMETER, Copenhagen, Denmark. From the shape of the polarization curves the kinetics parameters

Table 1 The composition of the tested steels

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 K and P figures

%H <sub>2</sub> O	Ol 37	Ol 50	Ol 60
	K/P	K/P	K/P
1	0,383/0,34	0,372/0,33	0,365/0,33
2	0,397/0,36	0,387/0,35	0,375/0,34
3	0,418/0,38	0,403/0,36	0,396/0,36
4	0,445/0,40	0,422/0,38	0,411/0,37
5	0,466/0,48	0,448/0,40	0,429/0,39

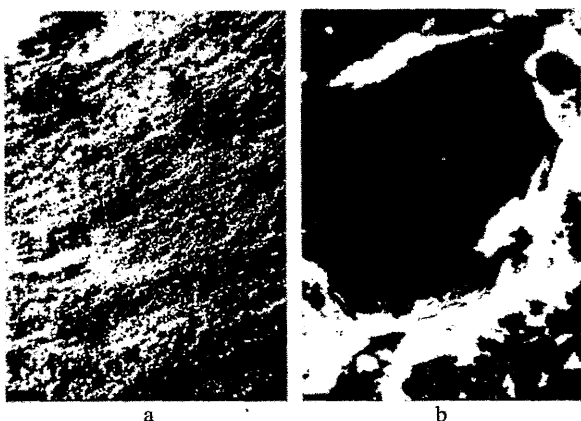


Fig.1 The metallic surface of the OL 60 sample in the system with 5 % water concentration (a x 60; b x 1200)

( $\epsilon_{st}$ ,  $\epsilon_{cor}$  and  $i_{cor}$ ) of the corrosion process were calculated.

The final corrosion 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 Yena diffractometer using Co(K $\alpha$ ) radiation, by IR spectroscopy on a SPECORD M82. The chemical composition (C, H, O and Fe) of the final compounds were also determined.

## Results and discussion

The value of the pH in the anhydrous system is 1.67. When water is added, the pH-value decreases until 1.60 – 1.61, fact proving that the dissociation process of the malonic acid occurs in organic solvents. If water is present, probably the H<sup>+</sup> ion is transferred from the solvent molecules to water molecules that have a higher polarity:

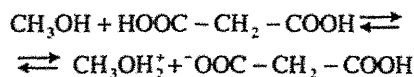


Table 3 The values of the kinetic parameters of the corrosion

Type of steel	$\epsilon_{cor}$ mV	$\epsilon_{st}$ mV	$i_{cor}$ $\mu\text{A}/\text{cm}^2$
Ol 37	-535	-550	28,08
OL 50	-525	-540	27,86
OL 60	-506	-535	26,28

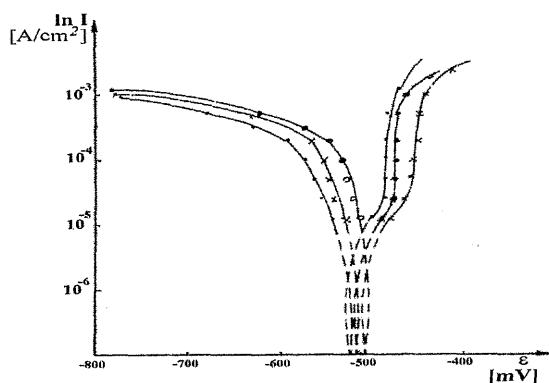
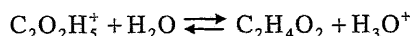
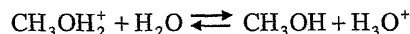
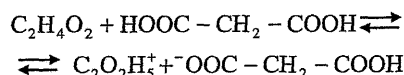


Fig 2 The polarisation curves in the system with 5 % water. (• OL 37 ; x OL 50 ; o OL 60)



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

From the presented data is observed that the corrosion rate increases with water concentration, because the oxyhydroxilic layer is not formed to assure the anticorrosive protection.

The metallic surface visualized by SEM presents for all steels, the pitting corrosion, unexpected for this type of organic acid. In the Fig.1, the metallic surface of OL 60 sample is presented.

The polarisation curves were plotted for 5 % water concentration and are shown in Fig.2.

From the aspect of these curves, an easy passivation tendency is observed for the values of potentials shown below:

$$\text{OL 37: } -535 \div -485 \text{ mV}$$

$$\text{OL 50: } -505 \div -465 \text{ mV}$$

$$\text{OL 60: } -525 \div -475 \text{ mV}$$

The values of the corrosion parameters are presented in Table 3.

From the values of density current is observed that the most stable steel is OL 60 with the higher carbon concentration, this behaviour is also explained by the smallest value for the weight loss.

The corrosion products are insoluble in the system at all water concentration and do not present X-ray diffraction spectra.

Table 4 The chemical composition of the corrosion compounds

%	OL 37	OL 50	OL 60
C	22,35	22,86	23,12
H	2,89	3,06	2,77
O	41,23	41,75	42,06
Fe	33,53	32,33	32,05

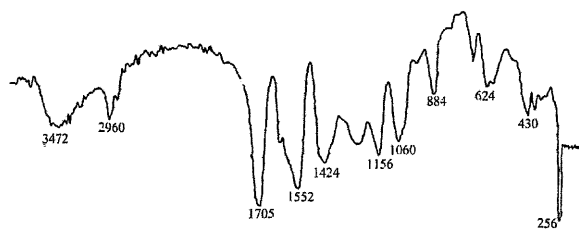


Fig 3 The IR spectrum of the corrosion compounds resulted from OL 60 in the system with 5 % water concentration

The IR-spectra of the corrosion compounds derived from the system with all different water concentration are identical, meaning that they present peaks at the same wave number. The IR absorption spectra of the corrosion compounds resulted from OL 60 in the system with 5 % water concentration is presented in Fig.3.

In this spectrum, two peaks are observed at  $256\text{ cm}^{-1}$  and  $430\text{ cm}^{-1}$ , both corresponding to Fe—O bonds, but the first is due to a strong bond and the second to a much weaker one. The value of the absorption peak for COO<sup>-</sup> group from malonic acid is displaced from value 1730 to  $1705\text{ cm}^{-1}$  that explains a stronger oxygen bonding. The displacement of the absorption peak of the HO<sup>-</sup> group contained in alcohol, from 1080 to  $1060\text{ cm}^{-1}$  also shows the oxygen participation in stronger bonding.

The peak situated at  $1860\text{ cm}^{-1}$  is specific for the HO<sup>-</sup> from the water molecules bounded in bridge bonding [14-15]. The other peaks from the IR spectrum are characteristic for the C—C and C—H rotation and vibration bonds [14-15].

Chemical elemental analysis of the corrosion compounds presents the same value for the constituents with an error smaller than 2 % for all resulted products in all the systems with different concentration. In Table 4, the media chemical composition of these compounds is presented.

This composition corresponds to a molecular rate Fe/malonate radical of 1/1 with a smaller iron content (< 3 %).

From the data presented the following corrosion mechanism is assigned:

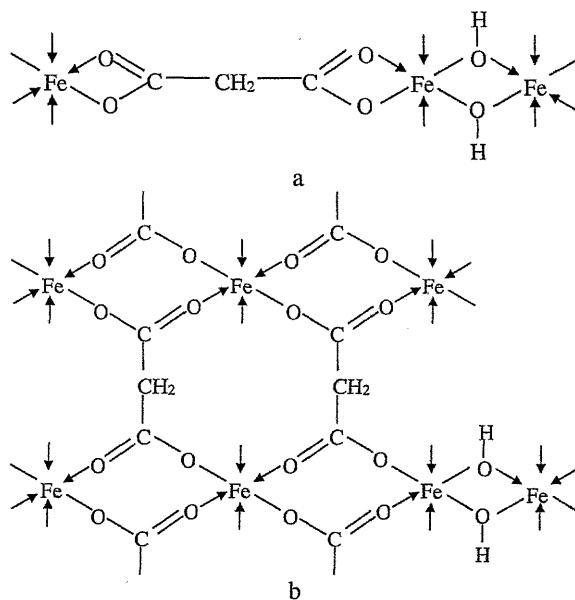
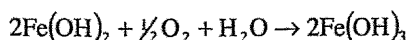
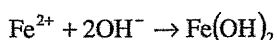
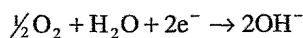
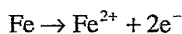
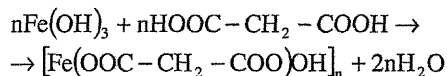


Fig.4 The structure of the corrosion compounds Fe(III) polymalonate. (a-linear; b-cyclic)



The structure of the polymer compound of iron with malonic acid is shown in Fig.4.

The hexacoordination of the Fe is determined by water molecules and/or by HO<sup>-</sup> groups in bridge bonding. Also, the polymer chain is accomplished by glycolate groups. Notable is also the fact that in literature indications is not specified the existence of a polymer malonate of iron or a basic malonate.

## Conclusions

- All steels types are corroded in the studied medium.
- The best behaviour is presented by the steel with the highest carbon concentration (0.4 %). That is due to the existence in the steel structure of the solid Fe—C solution that determines a superior stability of the material [16].
- Water is not used in the passive layer formation even if it is present in molar rates higher than 4/1 (when the system contain 4 % water the molar rate water/acid has the value 4.58/1). The fact that water does not participate in anticorrosive protection can be justified by the existence of two groups COO<sup>-</sup> in the structure of the acid that require a higher quantity of water in order to accomplish the oxyhydroxilic passive layer formation, using the O<sub>2</sub> dissolved.
- The corrosion mechanism is a complexing one with formation of insoluble compounds non-adherent on the surface of the corroded metal. These compounds presented an amorphous polymer structure.

- Remarkable is the fact that the malonic acid determines a pitting corrosion process.

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