

THE INFLUENCE OF WATER CONCENTRATION ON THE CORROSION OF LOW ALLOY STEELS IN THE SYSTEM METHANOL - ETHYLENE GLYCOL - N-BUTIRIC 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% n-butiric acid with water concentration between 1% to 5 %. The weight loss are measured and the gravimetric figure K ($\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) and the penetration figure P ($\text{mm}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$) are calculated. Also, the kinetic corrosion parameters are established. The methods used for identification and analysis of the corrosion compounds are: elemental analysis, I.R. spectra and X-ray diffraction. Also, by electron microscopy, a corrosion mechanism is assigned.

Introduction

This paper is a continuation of studies of the corrosion behaviour of low alloy steel types in methanol medium and/or ethylene glycol, having as corrosion reagent, saturated mono- and di-carboxyl organic acids [1-5]. This corrosion system and also the studied acids are the main responsible agents for the corrosion process that appears in the synthetic fiber industry.

Experimental

The three steel types studied for the corrosion are: OL 37, OL 50, and OL 60 having the chemical composition presented in *Table 1*.

The metallic samples used for corrosion were cut up from a cylindrical bar with 5 cm^2 active surface. A single basis of the cylinder was corroded after preliminary grinding and polishing. Dyeing protected the other basis and the lateral surface.

The corrosion system contained methanol, 10 % ethylene glycol and 5 % n-butiric acid, the water concentration varied between 1 % and 5 %. We used Merck reagents and the water was bidistilled, having electrical conductivity of 12 $\mu\text{s}\cdot\text{cm}^{-1}$. Karl-Fischer method was used to determine the water content. The variation of pH – values in the corrosion anhydrous

system and at different water concentration 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 corrosion system was open, allowing the permanent access of oxygen from the atmosphere, reproducing the industrial process conditions. The final weight loss was converted to gravimetric figures K ($\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) and penetration figures P ($\text{mm}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$).

For establishing the corrosion type, the metallic surface was visualised by electron microscopy on a TESLA B 300 microscope.

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

The corrosion final compounds, for every value of water concentration, were soluble in the system. They were obtained in solid state by evaporating the corrosive solutions at 40 °C, in inert atmosphere for avoiding the oxidation process that could take place because of the increasing temperature. After separation and drying, these compounds were analysed by X-ray diffraction on a HZG 4C Karl Zeiss Jena diffractometer using $\text{Co}(K_{\alpha})$ radiation, by IR spectroscopy on a SPECORD M82. The chemical composition (C, H, O and Fe) of the final compounds was also determined.

Table 1 The composition of steels used for corrosion test

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	0.303/0.27	0.293/0.26	0.286/0.26
2	0.312/0.28	0.307/0.28	0.293//0.26
3	0.325/0.29	0.315/0.28	0.305/0.27
4	0.306/0.27	0.301/0.27	0.287/0.26
5	0.301/0.27	0.295/0.26	0.273/0.25

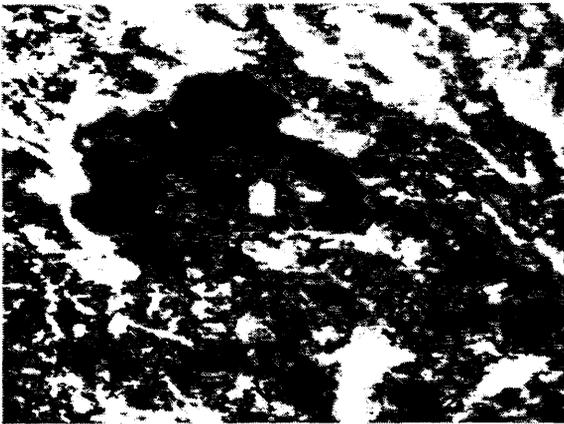


Fig.1 The metallic surface of OL 60 in the system methanol - ethylene glycol - n-butiric acid - 3% water (x 1200)

Results and discussion

Studying the pH - values, we observed that in anhydrous system, the pH value is 2.7 and adding water, it is very slowly decreased to 2.6, at 5% water concentration. This practically constant pH-variation showed that n-butiric acid ionisation occurred with the help of the two solvents. Water had not a significant importance in modifying the dissociation of the acid.

In Table 2, the values of weight losses converted into K and P figures are presented. From these values, we can observe a significant decrease the corrosion rate between 3 % and 4 % water concentration. This observation leads us to the conclusion that for values higher than 3 %, water molecules participate in the formation of passive oxyhydroxyde layer establishing. The metallic surface, visualised by electron microscope had the same aspect for all three types of steel, indicating a generalised corrosive process with a corrosive compound layer on the entire surface. This layer is not uniform, presenting holes, and cannot accomplish an efficient anticorrosive protection. In Fig.1, the aspect of the metallic surface of OL 60 in the system with 3 % water concentration, magnified by 1200 times is presented.

The polarisation curves were plotted for the values of 3% and 5% water concentration. They had the same

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

Types of steels	ϵ_{st}, mV		ϵ_{cor}, mV		$i_{cor}, \mu A/cm^2$	
	3%	5%	3%	5%	3%	5%
	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O
OL 37	-483	-427	-510	-440	2.03	1.32
OL 50	-467	-403	-480	-415	1.86	1.28
OL 60	-449	-395	-465	-410	1.73	1.05

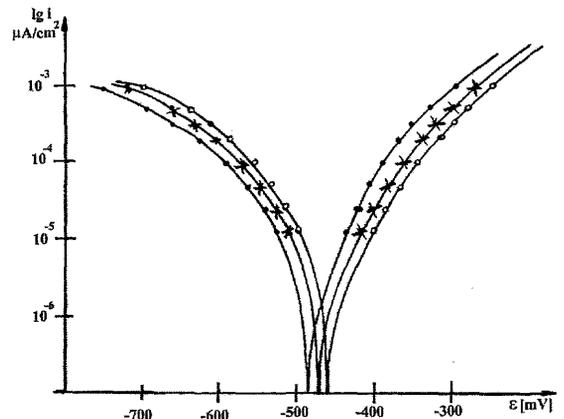


Fig.2 The polarization curves in the system methanol - ethylene glycol - n-butiric acid - 3% water (● OL 37; x OL 50; ○ OL 60)

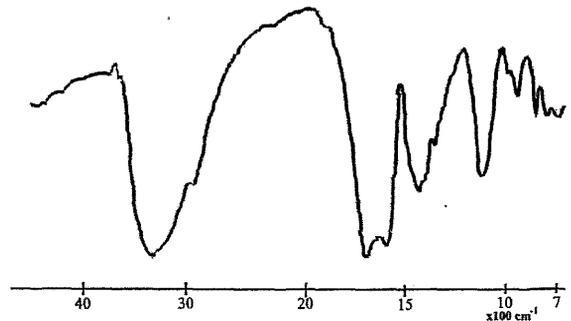


Fig.3 The IR spectra of the corrosion compounds obtained in the system methanol - ethylene glycol - n-butiric acid - 3% water

shape, as presented in Fig.2. From the shape of these curves, the kinetic corrosion parameters were calculated and presented in Table 3.

The value of the corrosion current density, that practically shows the corrosion rate, decreases after the 3 % water concentration in the system. This observation is in concordance with the determined value for the corrosion rate, observed by the weight loss.

Studying the values of weight losses and also of the corrosion current density, we observed that the steel with the best behaviour is OL 60.

In order to establish a corrosion mechanism, the final corrosion compounds were analysed.

The X - ray diffraction spectra of the corrosion compounds, of all types of steel, are the same and are being characteristic to the amorphous compounds.

Table 4 The chemical composition of the corrosion compounds in the system methanol - 10% ethylene glycol - n-butiric - 3% water

%	OL 37	OL 50	OL 60
C	42.17	42.86	42.56
H	7.04	7.35	6.87
O	28.56	28.47	23.03
Fe	22.23	21.32	21.54

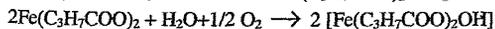
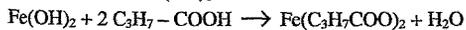
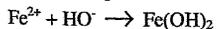
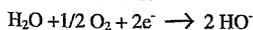
The IR - spectra are also identical, meaning that they present the same absorption bands at the same wave number; the IR-spectrum of the corrosion compound in the system containing 3 % water is presented in Fig.3.

In this spectrum, as it is mainly observed, the displacement of the characteristic peak of n-butiric acid, for the group COO⁻, from the value 1729 cm⁻¹ to 1690 cm⁻¹. This fact is explained by a stronger bonding of carboxylic oxygen. Also, the splitting in two peaks at this value explains the existence of two types of bonds, one covalent and the other coordinative [6]. The peak from 1550 cm⁻¹ shows that this group is asymmetrically bonded. The absorption bands of HO⁻ are placed at 3400 cm⁻¹ and 2900 cm⁻¹, case in which water is coordinative bonded through oxygen and also, they indicate that these groups participate to a bridge linkage Fe←O—Fe [7].

In the IR-spectrum, a peak at 1080 cm⁻¹ is also observed, characteristic for the OH groups, from alcohol [6-8]. The remaining maxima from the spectrum correspond to the vibration and rotation movements of C—C and C—H bonds.

The elemental chemical composition of the corrosion compounds is similar for all water concentrations (variation of 2 %). In Table 4, the chemical composition of the corrosion compound derived from the system with 3 % water is presented.

From the presented data the following mechanism is assigned:



The structure of iron(III) polybutirate is presented in Fig.4.

Also, it is very important to mention that in the studied references, were not found the data related to the compounds of iron with n-butiric acid.

The hexacoordination of iron and the bond of the final chain molecules are realised through CH₃O⁻ and HO—CH₂—CH₂—O⁻ groups.

Conclusions

- All three types of steel there is a given water concentration where the corrosion rate has a maximum value.

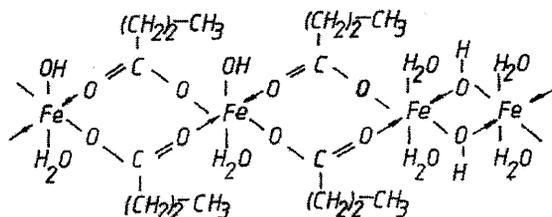


Fig.4 The structure of the polymer compound of the iron with the n-butiric acid

- The molar ratio water/acid, from which the corrosion rate decreases is 2.39, is smaller than the one presented in literature [9 - 11] for achieving an oxyhydroxylic passive layer. In literature, the value for this molar ratio is 4. The smaller value can be justified by the fact that the acid is dissociated in ions and, through the two organic solvents, water molecules are able to participate at smaller concentrations in the formation of the passive layer. This is in concordance with the minimum variation of pH, if into the system, more water is added.
- The steel with the highest stability in all the cases is OL 60, which has the highest carbon content; the stability may be connected to the existence in the steel structure of a solid iron-carbon solution, that is formed when the carbon concentration is grater than 0.3 % [12]. The corrosion mechanism is a complex one involving oxygen from the atmosphere.

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