CORROSION INHIBITION OF CrMo STEEL SURFACE IN 0.5 M H_2SO_4 + 5 mM PROPARGYLIC ALCOHOL SOLUTION

MIRKO GOJIĆ[1]*, LADISLAV KOSEC[2]

The inhibition of surface corrosion of low-alloyed CrMo steel by propargyl alcohol was investigated using the methods of linear polarization and electrochemical impedance spectroscopy (EIS). Tests were carried out in a deareated 0.5 M H_2SO_4 solution in the absence and in the presence of propargyl alcohol (5 mM) at different immersion times at open circuit potential. Propargyl alcohol suppressed both the anodic and cathodic dissolution processes by adsorption and by blocking of active sites. The inhibition efficiency increased as a function of immersion time. The agreement between the inhibition efficiency values calculated from the two types of measurement was quite good. The thickness of the inhibitory film (0.46-0.82 nm) was calculated from EIS measurements.

Key words: low-alloyed steel, corrosion inhibition, propargyl alcohol, inhibition efficiency

INHIBÍCIA POVRCHOVEJ KORÓZIE CrMo OCELE V ROZTOKU 0,5 M H_2SO_4+ 5 mM PROPARGYL ALKOHOLU

Študovali sme inhibíciu povrchovej korózie nízkolegovanej CrMo ocele propargyl alkoholom metódami lineárnej polarizácie a elektrochemickej impedančnej spektroskopie (EIS). Skúšky sme realizovali v roztoku koncentrovanej 0,5 M H_2SO_4 bez propargyl alkoholu a s propargyl alkoholom (5 mM) pri rôznych časoch ponorenia pod napätím. Propargyl alkohol potlačil tak anodický, ako aj katodický rozpúšťací proces adsorpciou a blokovaním aktívnych povrchov. Inhibičný účinok sa zvyšoval v závislosti od času ponorenia. Zistili sme dobrú zhodu medzi hodnotami inhibičného účinku, ktoré sme vypočítali z dvoch typov meraní. Hrúbku inhibičnej vrstvy (0,46–0,82 nm) sme vypočítali z EIS meraní.

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[1] Faculty of Metallurgy, University of Zagreb, Aleja narodnih heroja 3, 44103 Sisak, Croatia

[2] Faculty of Natural Sciences and Engineering, University of Ljubljana, Aškerčeva 12, 1000, Ljubljana, Slovenia

* corresponding author, e-mail: `gojic@siscia.simet.hr`

List of symbols

b_{c} – cathodic Tafel slope [mV/dec]
C_{dl} – double layer capacitance [F/cm^2]
C_{dl}^0 – capacity of uncovered steel surface [F/cm^2]
C_{dl}^1 – capacity of a completely covered steel surface [F/cm^2]
C_{dl}^{θ} – capacity to the steel surface at the different immersion time [F/cm^2]
E_{OC} – open circuit potential [V]
i_{corr} – corrosion current density [mA/cm^2]
L – inductance [H/cm^2]
R_{ct} – charge transfer resistance [$\Omega \cdot \mathrm{cm}^2$]
R_{el} – electrolyte resistance [$\Omega \cdot \mathrm{cm}^2$]
R_{p} – polarization resistance [$\Omega \cdot \mathrm{cm}^2$]
ε_{o} – vacuum dielectric constant [F/m]
ε_{r} – relative dielectric constant
δ_{org} – thickness of the protective layer [nm]
Q – constant phase element [$\Omega^{-1} \cdot \mathrm{S}^n \cdot \mathrm{cm}^{-2}$]
θ_{C} – surface coverage
θ_{LP} – inhibiting efficiency from linear polarization measurements
θ_{R} – inhibiting efficiency from impedance measurements

1. Introduction

Inhibitors of metal corrosion by acids act by retarding either the cathodic hydrogen reaction, or the anodic dissolution process, or both. The selection of inhibitor mainly depends on the type of acid, on its concentration, temperature and velocity of flow, on the presence even of minor amounts of dissolved inorganic and/or organic substances, and on the type of metallic material exposed to the action of acidic solution [1]. Acetylenic alcohols are considered to be an excellent class of inhibitors for corrosion and hydrogen embrittlement of steels in acidic environments [2–6]. The simplest among them is propargyl alcohol ($\mathrm{CH{\equiv}C\text{-}CH_2OH}$) (PA). Its protective effects are attributed to the chemisorption of its molecules on the metal surface through the electrons available from the triple bond [6], or to their polymerization on the metal surface where they form an adherent and continuous protective film [7, 8].

Very little investigative work has been done concerning the thickness of the protective film. Poling [9] has studied the growth of PA film thickness on the iron surface in hydrochloric acid solution. He claims that the film becomes highly protective only after it has grown to a thickness equivalent of many molecular layers. Our work was directed towards the establishment of conditions leading to the maximum coverage by a protective film of the low-alloyed CrMo steel electrode through comparison of the inhibition efficiencies of PA in sulphuric acid solution. In our investigation we used the methods of linear polarization and electrochemical impedance spectroscopy (EIS).

2. Experimental

Low-alloyed CrMo steel containing 0.41 % carbon, 1.01 % chromium and 0.70 % molybdenum [wt.%] was used in experiments. A sample 4 mm in diameter and 12 mm long was austenitized at 900 ℃ for 600 s by means of an LK.02

dilatometer and cooled with helium. After quenching to develop the martensite tempered microstructure, the specimen was tempered at 700 ℃ for 2400 s and then air cooled.

Electrochemical measurements were performed in a three-compartment glass cell. The working electrode was a CrMo steel rod with a 4 mm diameter embedded in a Teflon holder. The reference electrode was a saturated calomel electrode (SCE). A platinum gauze was used as counterelectrode.

The surface of the working electrode was polished with emery papers of Nos. 600, 800 and 1000. The electrode was degreased with ethanol under ultrasound, rinsed with doubly distilled water and dried at room temperature before use. The 0.5 M H_2SO_4 and 0.5 M H_2SO_4 + 5 mM PA solutions were prepared from reagent grade concentrated acid and doubly distilled water. Before measurements the working solution was bubbled with nitrogen for 30 minutes.

Linear polarization and impedance measurements were carried out on an EG & G PAR 273 potentiostat/galvanostat with a model 5301 lock-in amplifier. First the electrode was left at open circuit potential (E_{OC}) for 600 s, and after that it was polarized at −1.0 V for 120 s. Polarization curves were recorded at a scan rate of 1 $\mathrm{mV \cdot s^{-1}}$ in the potential range from −650 mV to the anodic potential limit $E = E_{\mathrm{OC}} + 15$ mV. EIS measurements were carried out for different immersion times at E_{OC} in the frequency range of 50 kHz–40 mHz at a rate of eight points per decade. All measurements were performed at 25±1 ℃.

3. Results and discussion

Fig. 1 shows polarization curves for CrMo steel in 0.5 M H_2SO_4 solution in the absence and in the presence of PA. The corrosion parameters calculated from the polarization curves are given in Table 1. The cathodic Tafel slopes (b_{c}) were evaluated using the standard procedure [10]. The corrosion current densities (i_{corr}) were estimated by Tafel extrapolation of the cathodic curve to the open-circuit corrosion potentials. Polarization resistance (R_{p}) was obtained over a range of ±20 mV with respect to E_{OC}. In this region, the relationship between the potential and the current was linear.

Table 1. Corrosion parameters from linear polarization measurements for low-alloyed CrMo steel in 0.5 M H_2SO_4 solution without and with 5 mM PA

c(PA) [mM]	E_{OC} [mV]	$-b_{\mathrm{c}}$ [$\mathrm{mV \cdot dec^{-1}}$]	i_{corr} [$\mathrm{mA \cdot cm^{-2}}$]	R_{p} [$\Omega \cdot \mathrm{cm^2}$]
0	−465	122	0.349	56
5	−435	160	0.094	278

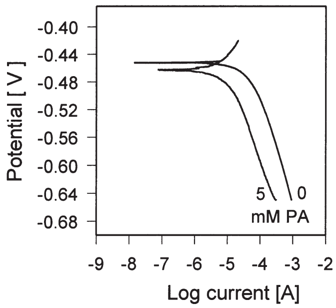

Fig. 1. Linear polarization curves of low-alloyed CrMo steel in 0.5 M H_2SO_4 and 0.5 M H_2SO_4 + 5 mM PA solutions.

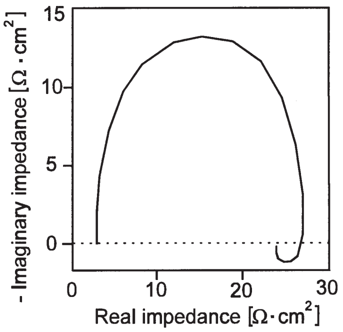

Fig. 2. Nyquist plot of low-alloyed CrMo steel in 0.5 M H_2SO_4 solution at open circuit potential.

A positive shift in E_{OC} (Table 1) proved PA to be an effective suppressor of the anodic dissolution reaction. However, the polarization curve in Fig. 1 showed that PA also suppressed the hydrogen evolution reaction on CrMo steel. Data in Table 1 demonstrate an increase in the b_{c} value comparable to that following the addition of 5 mM PA to 0.5 M H_2SO_4 solution. This would suggest that PA may also alter the mechanism of hydrogen evolution reaction on the CrMo steel surface. Similar results have been reported for PA in the case of iron [11]. The inhibition efficiency is directly proportional to the amount of inhibitor adsorbed or to the degree of surface coverage. The inhibition efficiency from linear polarization measurements (θ_{LP}) was defined as:

$$\theta_{\mathrm{LP}} = \frac{i^0_{\mathrm{corr}} - i_{\mathrm{corr}}}{i^0_{\mathrm{corr}}}, \tag{1}$$

where i^0_{corr} and i_{corr} are corrosion current densities in the absence and in the presence of PA. In the presence of 5 mM PA in 0.5 M H_2SO_4 solution the inhibition efficiency was about 0.73.

The corrosion behaviour of low-alloyed CrMo steel in the absence and in the presence of 5 mM PA at E_{OC} was investigated by the EIS method. Figs. 2 and 3 show Nyquist plots of CrMo steel in uninhibited and inhibited systems for different immersion times at E_{OC}. A fitting procedure was carried out using the nonlinear least squares computer program developed by Boukamp [12]. The impedance spectra were modelled with equivalent electrical circuits shown in Fig. 4 where R_{el} is the electrolyte resistance, $\mathrm{R}_1 + \mathrm{R}_2$ is the charge transfer resistance (R_{ct}), L is inductance, Q is the constant phase element (CPE), and C_{dl} is the double layer

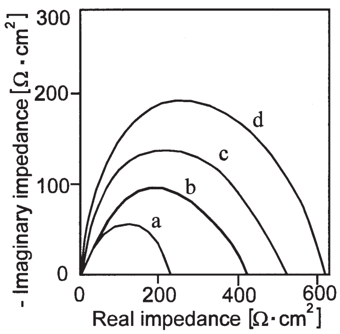

Fig. 3. Nyquist plots of low-alloyed CrMo steel for different immersion times at open circuit potential in 0.5 M H_2SO_4 + 5 mM PA solution: a – 0 hour, b – 0.5 hour, c – 1 hour, d – 2 hours.

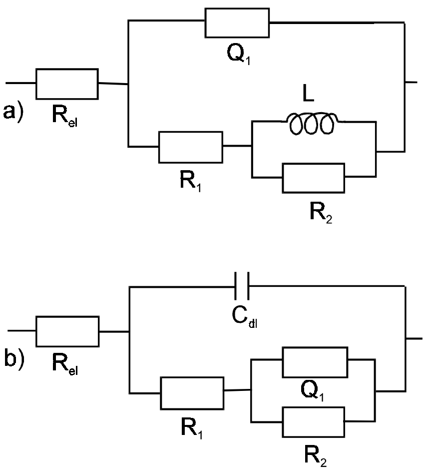

Fig. 4. Schematic illustration of electrical circuits for low-alloyed CrMo steel in 0.5 M H_2SO_4 (a) and 0.5 M H_2SO_4 + 5 mM PA solutions (b).

capacitance. The constant phase element (Q) is a combination of properties related to the surface and electroactive species [13]. The corresponding parameters of equivalent electrical circuits are given in Table 2.

Table 2. Parameters of electrical circuits for low-alloyed CrMo steel in 0.5 M H_2SO_4 solution without and with 5 mM PA obtained by analysis of the impedance spectra

c(PA) [mM]	Immersion time [hours]	R_{el} [$\Omega\cdot\text{cm}^2$]	$Q_1 \times 10^6$ [$\Omega^{-1}\cdot\text{S}\cdot\text{cm}^{-2}$]	n_1	R_1 [$\Omega\cdot\text{cm}^2$]	L [$\text{H}\cdot\text{cm}^{-2}$]	R_2 [$\Omega\cdot\text{cm}^2$]	C_{dl}^{θ} [$\mu\text{F}\cdot\text{cm}^{-2}$]
0	0	0.9	718.0	0.77	26.0	143	7.0	
5	0	1.4	508.4	0.78	3.4		214.6	31.1
	0.5	1.5	456.6	0.82	2.8		439.2	38.0
	1.0	0.9	405.2	0.70	5.6		507.8	26.2
	2.0	0.8	296.0	0.70	9.4		687.6	21.7

The character of the impedance spectra taken at E_{OC} in the absence of PA differed from the one recorded in its presence. The spectra in the absence of PA

(Fig. 2) included faradaic inductive impedance. This behaviour can be explained by the process of relaxation of adsorbed intermediates at E_{OC} [14, 15]. When 5 mM PA was added to 0.5 M H_2SO_4 solution the system was well inhibited (Fig. 3), the inductive behaviour disappeared and only capacitive loops were observed at the lowest frequencies (40 mHz). The R_{ct} values increased with increasing immersion time due to adsorption of PA molecules (Fig. 5). The corrosion current density (i_{cor}) was inversely proportional to R_{ct}. Thus, at a higher R_{ct} value the CrMo steel electrode had a lower corrosion rate. The strongest effect was observed for the immersion time of two hours with R_{ct} values of 697 $\Omega \cdot \mathrm{cm}^2$. The inhibition efficiencies based on the impedance data (θ_{R}) were calculated using the equation:

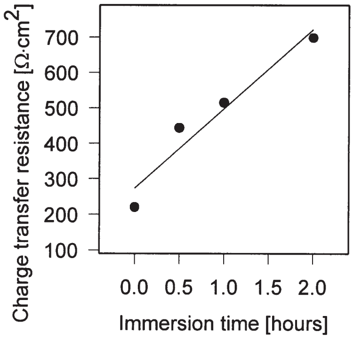

Fig. 5. Effect of the immersion time of low-alloyed CrMo steel at open circuit potential in 0.5 M H_2SO_4 + 5 mM PA solution on the charge transfer resistance.

$$\theta_{\mathrm{R}} = \frac{R^i_{\mathrm{ct}} - R_{\mathrm{ct}}}{R^i_{\mathrm{ct}}}, \tag{2}$$

where R^i_{ct} and R_{ct} are the charge transfer resistances in the presence and in the absence of PA. With longer immersion times more PA molecules get adsorbed and the protective film exhibits a proportional growth until saturation occurs. This fact supports the observed decrease in C_{dl} values in EIS measurements at E_{OC} (Table 2). The decrease in C_{dl} values was due to the adsorption of PA on the steel surface. The adsorption of PA on the CrMo steel surface can occur directly on the basis of donor-acceptor interactions between the π-electrons of the PA and the vacant d-orbitals of iron surface atoms as proposed by Bartos et al. [6]. An equation relating the C_{dl} values to the degree of surface coverage from impedance measurements based on capacitance (θ_{C}) has been given by Dus and Szklarska-Smialowska [16]:

$$\theta_{\mathrm{C}} = \frac{C^0_{\mathrm{dl}} - C^\theta_{\mathrm{dl}}}{C^0_{\mathrm{dl}} - C^1_{\mathrm{dl}}}, \tag{3}$$

where C^0_{dl} denotes the capacity corresponding to an uncovered steel surface ($\theta = 0$), C^1_{dl} refers to the capacity corresponding to a completely covered steel surface ($\theta = 1$), and C^θ_{dl} is the capacity corresponding to the steel surface to be studied (in 0.5 M H_2SO_4 + 5 mM PA at different immersion times (Table 2)). For C^0_{dl} in Eq. (3), we used the C_{dl} value of iron in 0.5 M H_2SO_4 solution, i.e. 105.0 $\mu\mathrm{F} \cdot \mathrm{cm}^{-2}$

[17], and for C_{dl}^{1} the C_{dl} value from EIS measurements in 0.5 M H_2SO_4+ 5 mM PA at the immersion time of two hours (see Table 2), i.e. 21.7 $\mu F\cdot cm^{-2}$. The θ_{LP}, θ_{R} and θ_{c} values are given in Table 3. Increase in immersion time of CrMo steel at E_{OC} in 0.5 M H_2SO_4 + 5 mM PA always induced a large increase in inhibition efficiency. The high inhibition efficiency values showed PA to be an effective corrosion inhibitor for CrMo steel in sulphuric acid solution. There was a small difference between the inhibition efficiency values calculated from linear polarization measurements and those from EIS measurements. The difference arose as a result of longer duration of impedance measurements (17 minutes). An agreement of θ_{R} and θ_{C} values gives evidence that Eq. (3) is characteristic of the inhibitory properties of PA.

Table 3. The inhibition efficiencies calculated from linear polarization and impedance measurements for low-alloyed CrMo steel in 0.5 M H_2SO_4 + 5 mM PA solution

c(PA) [mM]	Immersion time [hours]	θ_{LP}	θ_{R}	θ_{C}
5	0	0.73	0.84	0.88
	0.5		0.92	0.80
	1.0		0.93	0.94
	2.0		0.95	1.00

The double layer capacitance reflects the thickness of the layer of PA molecules adsorbed. The thickness of the protective layer (δ_{org}) was calculated from the following equation:

$$\delta_{\mathrm{org}} = \varepsilon_0 \varepsilon_{\mathrm{r}} / C_{\mathrm{dl}}^{\theta}, \qquad (4)$$

where ε_0 is the vacuum dielectric constant ($8.854\cdot 10^{-12}$ F$\cdot$m^{-1}), ε_{r} is the relative dielectric constant and C_{dl}^{θ} is the double layer capacity of the steel electrode at a given immersion time in 0.5 M H_2SO_4 + 5 mM PA at E_{OC} (see Table 2). The ε_{r} is taken to be 20 [18]. By increasing the immersion time of CrMo steel in 0.5 M H_2SO_4+ 5 mM PA at E_{OC} the thickness of the protective film increased from 0.46 to 0.82 nm (Fig. 6). Our results are in accordance with the conclusions of Rauscher et al. [19] that the improved inhibition efficiency with

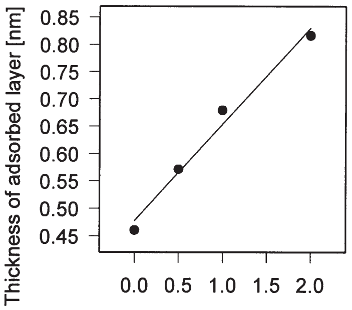

Fig. 6. Effect of the immersion time of low-alloyed CrMo steel at open circuit potential in 0.5 M H_2SO_4 + 5 mM PA solution on the thickness of adsorbed layer.

PA can be attributed to the thickening of the film. However, it is likely that more and more PA molecules get adsorbed and that the protective layer grows linearly with immersion time until saturation occurs.

4. Conclusion

From the results of linear polarization and EIS measurements of corrosion inhibition on low-alloyed CrMo steel surface in deareated 0.5 M H_2SO_4 + 5 mM PA solution at E_{OC} the following conclusions can be drawn:

1. PA suppresses both the anodic and cathodic reactions. Thus PA acts as a mixed inhibitor for the low-alloyed CrMo steel in 0.5 M H_2SO_4 solution.

2. There is a relationship between the inhibition of the steel surface corrosion and the adsorption of PA molecules. This is confirmed by increase in charge transfer resistance (R_{ct}) and decrease in double layer capacitance (C_{dl}) values.

3. The inhibition efficiency increases with increase in the immersion time of low-alloyed CrMo steel at E_{OC} in the test solution. The results of linear polarization measurements are in agreement with those of EIS tests.

4. The thickness of the protective film calculated from EIS measurements increased from 0.46 to 0.82 nm during the testing up to two hours at E_{OC}.

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Received: 15.2.2002