

The Effect of Alcohol on the Passivation of Al Alloys in 1 N H₂SO₄ Solution

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Abstract—In this study, the influence of different alcohol on the passivation of aluminium alloys have been investigated by using current-potential curves. Experimental results show that the addition of alcohol in H₂SO₄ solution have been changed passivation potential distance of the alloys. Elemental compositions of alloys have also directly affected passivation of alloys. This influence is more effective especially in alloys content higher Si also and less Cu.

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1. INTRODUCTION

Aluminium is extensively used in various industrial operations and the study of its corrosion inhibition in pickling baths is of great importance. Therefore, the inhibition of aluminium corrosion in acid solutions by organic additives has been studied in a considerable detail [1–6]. Aluminum and aluminum alloys lend themselves to many engineering applications because of their lightness combination with strength, their high corrosion resistance, their thermal and electrical conductivity and low cost. The main applications of these materials are in aeronautical, automotive and food industries. Compared to pure aluminum, its alloys are endowed with better mechanical properties but with lower corrosion resistance. On the other hand, alloying elements such as copper, zinc, magnesium and silicon added to aluminum, improve mechanical properties but frequently reduce localized corrosion resistance, in particular, pitting and exfoliation corrosion. Stronger localized attack on alloys in comparison with aluminum has been ascribed to alloy surface micro structural heterogeneity [7–12].

Gojic et al. (2001) stated the effect of propargylic alcohol (PA) on the corrosion inhibition of low alloy CrMo steel in sulphuric acid at the open circuit potential E_{OC} was investigated by DC-polarization and AC-impedance spectroscopy measurements, respectively. It was found that the addition of PA induced the positive shift of E_{OC} and the decreasing of cathodic currents. The anomalous Tafel cathodic slopes were explained using a modified adsorption-interaction model. The inhibition process was treated as the substitutional adsorption process. The adsorption of PA was fitted well by means of Flory-Huggins isotherm.

The standard free energy of adsorption of PA was calculated (-15 kJ mol^{-1}). Gonçalves et al. (2002) reveals that the electrochemical behaviour of copper, nickel and copper/nickel (Cu55/Ni45) alloy in 0.5 M H₂SO₄ in the absence and presence of propargyl alcohol has been studied. The results indicate that the electrochemical behaviour of the copper/nickel alloy similar to that of nickel. The interaction between the electrode surface and the organic compound is a relatively fast process and depends on the adsorption potential and alcohol concentration. Anodic currents associated with the electrooxidation of the metals decrease in the presence of propargyl alcohol. Differences in inhibition experience by the three electrodes are discussed in terms of cyclic voltammetry, potentiometry and impedance measurements. Jayaperumal et al. (2000) in their study deals with the evaluation of inhibition effect of ethanolamines on oil well tubular materials of grade N-80 steel in 15 per cent hydrochloric acid at room temperature with 0–2 percent amine concentrations. The amines such as mono, di and triethanolamine were studied for their inhibiting capacity by mass loss method, DC polarization method and AC Impedance method. The inhibitor efficiency increases with increasing concentration of amines. Monoethanolamine is found to be more effective than the other two amines. Patermarakis and Moussoutzannis (2002) investigated that equations describing the mass and charge transport phenomena and composition of the solution at pore bases during the regular/uniform growth of porous anodic alumina films in pure H₂SO₄ solution were suitably solved to describe them in H₂SO₄, Al₂(SO₄)₃ solution. The current densities at which the H₂SO₄ concentration becomes minimum at low film thicknesses were determined which coincided with the experimental ones above of which

¹ The article is published in the original.

Table 1. Chemical composition [wt] of the alloys studied in the present work

Alloy	Cu	Mg	Si	Fe	Mn	Ni	Zn	Pb	Sn	Ti	Cr
E 110	3.10	0.29	5.20	0.47	0.35	0.03	0.19	0.04	0.001	0.03	0.008
E 140	0.85	0.20	12.00	0.64	0.38	0.09	0.48	0.06	0.001	0.03	0.01
E 150	2.35	0.23	12.30	0.82	0.26	0.08	0.58	0.04	0.02	0.03	0.01
E 160	3.40	0.22	8.60	0.88	0.21	0.09	0.75	0.09	0.02	0.03	0.01
E 171	0.24	0.48	10.00	0.44	0.38	0.008	0.23	0.01	0.005	0.02	0.01
E 195	0.94	1.02	18.23	0.23	0.011	0.97	0.004	—	—	0.01	0.002

pitting appears. They decreased with the $\text{Al}_2(\text{SO}_4)_3$ concentration. A theory was formulated explaining the promoting effect of sulphate additives on pitting appearance which is important to develop methods for producing regularly grown high quality films. Quraishi and Sharma (2002) has been synthesized a new corrosion inhibitor namely 4-amino-3-butyl-5-mercapto-1,2,4-triazole (ABMT) and its inhibitive performance towards the corrosion of mild steel in 1 N sulphuric acid (H_2SO_4) investigated by weight loss and potentiodynamic polarization techniques. Potentiodynamic polarization measurements clearly reveal that the investigated inhibitor is of mixed type. The adsorption of the inhibitor on the metal surface in the acid solution was found to obey Temkin's adsorption isotherm. The aluminium alloys were used in our previous study related to the industrial alloys. The corrosion of these alloys determined by the Tafel's extrapolation and linear polarization methods and the effect of different alcohols on the corrosion of these alloys were studied in these studies [22–24]. It is concluded that alcohol leads to a decrease in the corrosion of aluminium alloys in acidic media. Therefore in this study, Al alloys were examined behaviour of passivity of aluminium alloys by using cyclic voltametry technic in 1 N H_2SO_4 and 1 N $\text{H}_2\text{SO}_4 + 20$ mM alcohol solutions. Alcohols used for this study are 1-buten 3-ol (1b3ol), 2-methyl 3but 2-ol (2m3b2ol), 3-methyl 2-buten 1-ol (3m2b1ol), 3-methyl 3-buten 1-ol (3m3b1ol), 3-methyl 1-penten 3-ol (3m1p3ol), and 5-hexen 1-ol (5hexen1ol).

2. EXPERIMENTAL

All the chemicals were purchased from Merck and used without any further purification. All the experiments were carried out open to the atmosphere, under room temperature conditions. A conventional three-electrode set up was used for the experiments. The counter electrode was a platinum wire, a saturated calomel electrode (SCE) was used as the reference and all the potential values were referred to this electrode. The alloys samples were cylindrical rods with 0.3 cm diameter. The working electrode area was one of the bottoms of cylinder, while the rest of electrode was embedded in thick polyester block. In order to remove any existing passive film, the surface of working elec-

trodes were polished using up to 1200 grade emery paper prior to each experiment, and washed with bi-distilled water. The synthesis of alcohol film on Al alloys was achieved by using cyclic voltammetry technique. The anodic polarization curves were recorded after 20 minute of immersion time in corrosive test solution. The scan rate is 20 mV/s. In this study, Wenking PGS 2000D potentiostat, Pentium IV computer and 1020 HP printer were used in electrochemical experiments. The chemical compositions of the studied Al alloys are given Table 1.

3. RESULTS AND DISCUSSIONS

Current density-potential curves of alloys obtained with 20 mV/s scanning rate in 1 N H_2SO_4 and 1 N $\text{H}_2\text{SO}_4 + 20$ mM alcohol solutions were shown in Fig. 1.

The current density value remained almost around zero from -0.6 to 1.0 V. Then, the current value started to increase continuously due to oxygen gas evolution.

The passivity current densities of each alloys obtained 1 N H_2SO_4 and 1 N $\text{H}_2\text{SO}_4 + 20$ mM alcohol solutions at 1000 mV (SCE) were given in Table 2.

When the Table 2 is examined, it is seen that alcohol addition shifted the current densities of passivity. This shows variability depending on the structure of alcohol. As it is mentioned before the adsorption of substance in outer porous layer plugs the porous and slows down the corrosion if the size of alcohol molecule is small (Büyüksağış and Aksüt, 2002,a). If there is a desorption on the surface, the occurrence of new oxide layer (or resulted from desorption) and the increasing of current are performed. The lowest passivity current densities can be observed on E171 in Table 2. While the substances in the structure of E195 alloy get oxidized, they decrease in reverse scan (Fig. 2).

The alcohols on E195 cover the surface well and there is a current increase (oxidation) at 0 V (Fig. 2). The passivity current is small and 3-methyl-2-buten-1-ol reduced in -400 mV (Fig. 2).

Oxygen occurs in higher potential by water reduction. Metal dissolution occurs either alcohol oxidation or desorption. The inhibition is high in H_2SO_4 acid solution and as a result of this the passivity current is low. The fact that the reverse scan of all the anodic

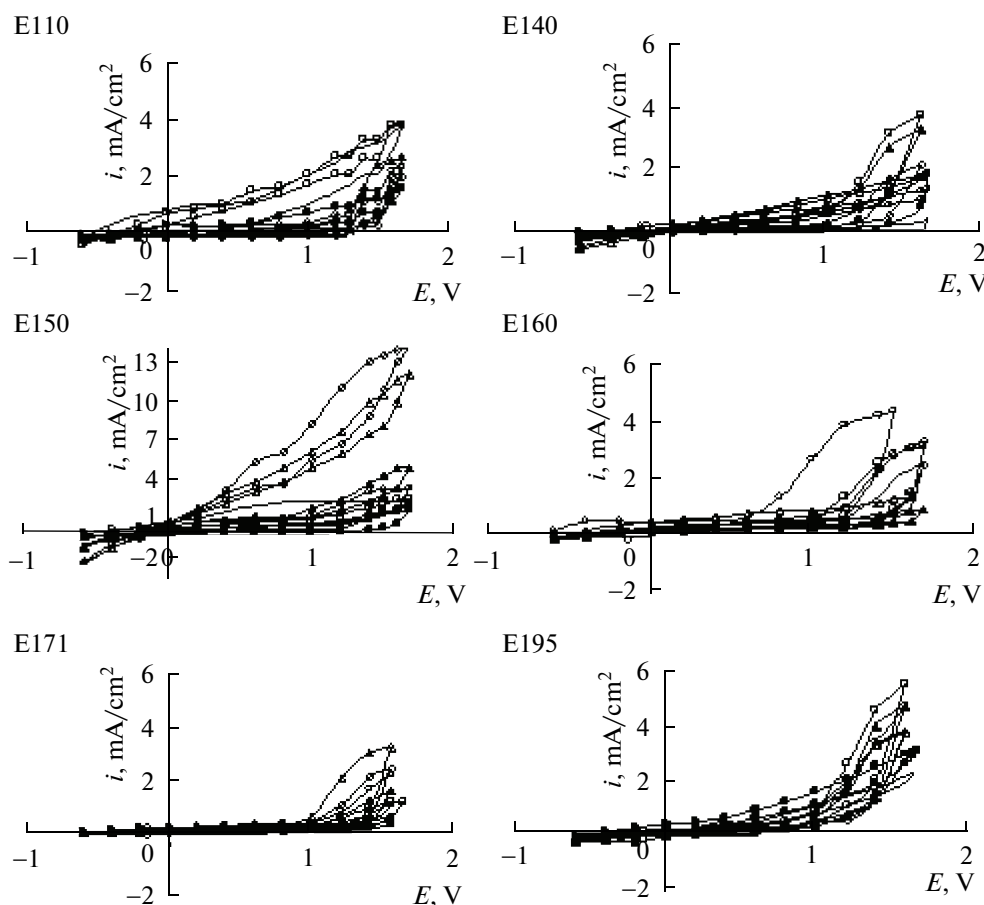


Fig. 1. Current density-potential curves of alloys obtained in 1 N H_2SO_4 and 1 N H_2SO_4 + 20 mM alcohol solutions. @ H_2SO_4 , @ 1b3ol, @ 2m3b2ol, @ 3m2b1ol, @ 3m3b1ol, @ 3m1p3ol, @, Shexen1ol.

curves are almost the same indicates that alcohols oxidized. The increase of the current shows in the presence of 1-buten-3-ol on E140 alloy alcohol is not adsorbed, on the contrary, it is desorbed easily (corrosion rate must be fast) or oxidized. The same case is valid for 3-methyl-2-buten-1-ol. 3-methyl-1-pentyn-3-ol decrease the passivity current in E110 alloy, so that it covers the surface very well in H_2SO_4 acid solution (Fig. 2). New surface layer occurs in E171 after +400 mV and the transpassivity starts in

+1200 mV (Fig. 11). Surface layer growth does not occur in E150 (in the medium with inhibitor). Bigger passivity currents, show a growth of layers in the medium without inhibitor (Fig. 2, Table 2).

Increasing of current density was related to the oxidation of alcohol. When the potential value reached +0.6 V was occurred a first anodic current peak at the reverse scan, a cathodic peak appeared at around +0.80 V. This peak is related to the reduction product of alcohol on the metal surface. Increasing film resis-

Table 2. The passivity current densities of alloys 1 N H_2SO_4 and 1 N H_2SO_4 + 20 mM alcohol solutions at the 1 V potential

	H_2SO_4	1b3ol	2m3b2ol	3m2b1ol	3m3b1ol	3m1p3ol	Shexen1ol
	i (mA/cm ²)	i (mA/cm ²)	i (mA/cm ²)	i (mA/cm ²)	i (mA/cm ²)	i (mA/cm ²)	i (mA/cm ²)
E 110	2.15	—	2.19	0.51	0.17	0.87	0.47
E 140	0.12	1.16	0.68	0.79	0.26	0.14	0.78
E 150	0.26	6.23	1.32	1.44	8.42	0.44	2.01
E 160	0.62	0.89	0.64	2.76	0.76	0.47	0.47
E 171	0.14	0.64	0.31	0.38	0.37	0.22	0.34
E 195	1.13	0.96	0.96	0.37	0.89	1.70	0.71

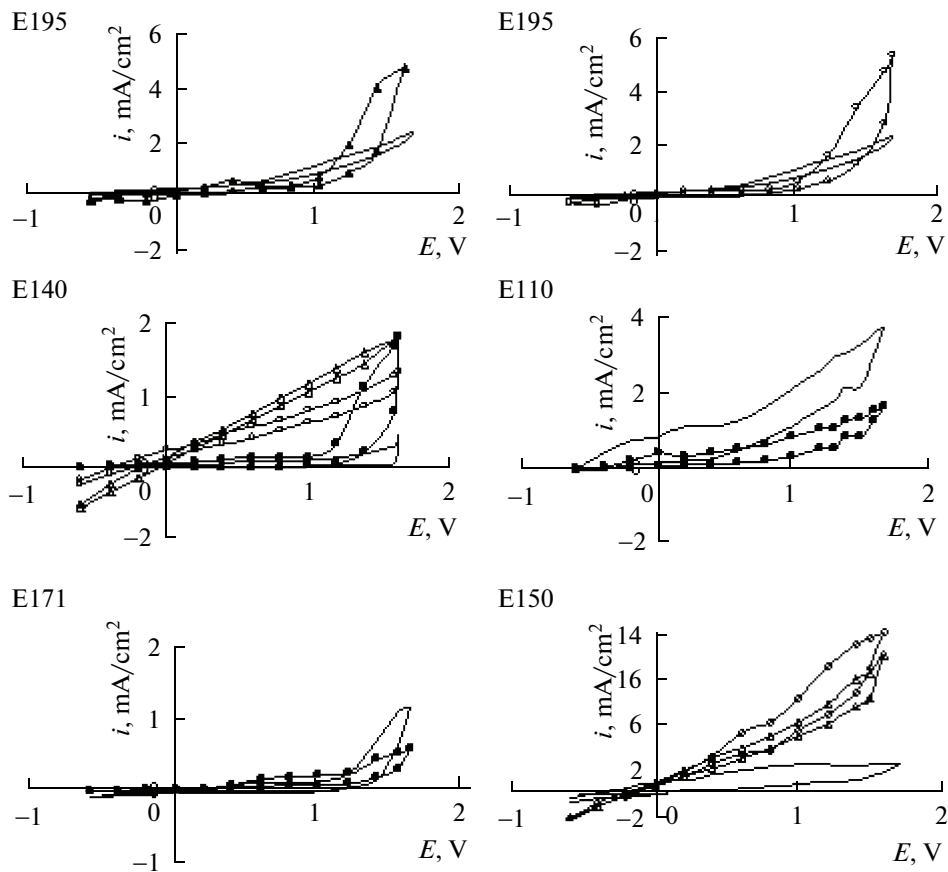


Fig. 2. Current density-potential curves of alloys obtained in 1 N H₂SO₄ and 1 N H₂SO₄ + 20 mM alcohol solutions. @ H₂SO₄, @ 1b3ol, @ 2m3b2ol, @ 3m2b1ol, @, 3m3b1ol, @ 3m1p3ol, @ 5hexen1ol.

tance due to polymerization of alcohol on the metal surface or accumulation of corrosion products within the pores [25]. When the Table 2 is examined, it is seen that alcohol addition shifts the passivity current and the passivity potential of dissolution to more noble values. This case shows variability depending on the structure of alcohol. As it is mentioned adsorbed substance plugs before porous layer and slows down the corrosion if the size of alcohol molecule is small [24], the lowest passivity current densities can be observed (E171 Table 2).

CONCLUSIONS

As a result of these study, it is observed that adding alcohol into 1 N H₂SO₄ solution interval of the passivity potential significantly changes depending on the alloys composition.

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FIGURE CAPTIONS