## PHYSICOCHEMICAL PROBLEMS OF MATERIALS PROTECTION

# Effect of Alcohol on the Corrosion of Al Alloys in 1 N H<sub>2</sub>SO<sub>4</sub> Solution Part I

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Abstract—The aim of this paper is to examine the effects of alcohol (1-buten–3-ol-l, 2-methyl–3-butyn–2-ol, 3-methyl–2-buten–1-ol, 3-methyl–1-pentyn–3-ol, 5-hexen–1-ol) on the corrosion of Al alloys. The inhibiting effect of alcohol was investigated by electrochemical current-potential curves, atomic absorption spectrometry (AAS), metal microscopy,SEM and EDS. The results showed that alcohol (1-buten–3-ol, 2-methyl–3-butyn–2-ol, 3-methyl–2-buten–1-ol, 3-methyl–3-buten–1-ol, 3-methyl–3-buten–1-ol, 5-hexen–1-ol) had an inhibiting effect on the corrosion of aluminium alloys. Experimental results show that corrosion of alloys in  $H_2SO_4$  solution have been effected by elements in alloys such as Cu, Zn, Mg and adsorption of alcohol on the surface of alloys in  $H_2SO_4$  solution obeys Temkin adsorption isotherm. The use of alcohol in  $H_2SO_4$  solution were shifted corrosion potentials ( $E_{cor}$ ) to more negative values and acted as cathodic inhibitors on the aluminum alloys. EDS analysis of alloys displayed different intermetallic compounds on the surface of alloys. This paper has showed that these alcohol inhibited corrosion of aluminium alloys in  $H_2SO_4$  solution. The concentration of 20 mM alcohol was shown that above 90% inhibition was achieved, which is a rather high value.

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#### **INTRODUCTION**

Aluminum and its alloys are used commercially as electronic, aerospace, packaging and architectural materials due to their low density and relatively high corrosion resistance. One of the important features of Al is the ready formation of an air-formed oxide which can be thickened by anodizing [1, 2]. The importance and wide range of applications of Al and its alloys have led to both intensive and extensive research into the electrochemical behavior of these materials in a variety of media. It seems to be important to investigate the corrosion processes occurring in solutions of different pH and to understand the role of inhibitors usually used for the inhibition of Al corrosion [3]. Corrosion and passivation of aluminum and its alloys is a subject of tremendous technological importance due to increased industrial applications of these materials [4, 5].

#### **EXPERIMENTAL**

**SEM-EDS and Metal Microscopy.** Microphotograph from the surface and EDS analysis of alloys have been obtained by using JEOL/EO JSM 5600 SEM and ZEISS AXIOPHAT metal microscopy. Before that microphotograph the surface of alloys have been prepared metallographic methods. Each alloy firstly have been ground from rough emery paper to fine emery paper (120, 240, 320, 400, 600, 800, 1000, 1200 grit paper) by using Metkon Gripo 2V Grinder Polisher (250–300 tour or period/min). Then alloys have been polished with alumina and washed using pure water. And then alloys have been washed with alcohol and dried warm air current. Alloys were placed in resin mold. Microphotograph from the surfaces were took photographs SEM and metal microscopy and also EDS analysis were made on this samples.

*Current-potential curves.* As working electrodes Al–Cu–Si alloys, pure Al, pure Zn, pure Cu and pure Mg metals were used. The experiments were carried out in a electrochemical cell with a working electrode, a platinum electrode and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively. All potentials were referred to the saturated calomel electrode. The chemical compositions of the studied Al alloys are given Table 1.

Al alloys were 3 mm in diameter and mounted in teflon. Before each experiment the electrodes were polished with 1200 grit emery paper, washed thoroughly with bidistilled water, then transferred to the cell. All solutions were de-areated with nitrogen for 30 min in the cell before the experiment The nitrogen was thoroughly purified oxygen with pyrogallol. During each experiment, solutions were mixed with a magnetic stir-

**Table 1.** Chemical composition [wt] of the alloys

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

rer. Solutions were prepared bidistilled water using Merck grade  $H_2SO_4$ , HCl and alcohols.

Measurements were obtained using a system consisting of a Wenking PGS 2000D potentiostat, Pentium 100 computer and 845 C HP printer. To determine the corrosion rates, the anodic and cathodic Tafel regions extrapolating to corrosion potentials were used. The polarization resistance values were calculated from linear zones of current-potential curves near the corrosion potentials. Results were always repeated at least three times.

Atomic absorption spectrometry (AAS). During the experiment the amounts of dissolved elements (Al, Cu, Mn, Fe, Zn, Mg) passing to the solution from the surface of studied alloys have been determined by using VISTAX PCD Simolt Aneous AAS. AAS analysis have been determined in 1 N H<sub>2</sub>SO<sub>4</sub> solution and 1 N H<sub>2</sub>SO<sub>4</sub> + 20 mM alcohol solutions. 3-methyl–1-pentyn–3-ol has been choiced showing good inhibition from alcohol. Electrode were plunged to electrochemical cell that containing studied solution. From the electrochemical cell were passed 24 hour N<sub>2</sub> gases and during was mixed solution.

#### RESULTS

*Microphotograph of SEM and Metal Microscopy and EDS analysis.* Microphotograph on the surface of alloys were imaged SEM and metal microscopy. In addition to the effect of structure surface of alloys and compositions were determined by EDS. EDS analysis were given Table 2. Microphotograph of SEM and metal microscopy were given Figs. 1–2,

*Current-potential curves.* Figure 3 give the anodic and cathodic potentiodynamic polarization curves 1 N  $H_2SO_4$  in the absence and presence of various concentrations of 1-buten—3-ol alcohol for E–150 aluminium alloy.

Al alloys in 1 N  $H_2SO_4$  solution and addition this solution 0.2; 1, 2, 20 mM alcohols obtained corrosion characteristics were given in Tables 3–5.

To obtained inhibition percentage efficiency values  $(\theta)$  in H<sub>2</sub>SO<sub>4</sub> solution containing 0.2; 1, 2, 20 mM alcohols were changed the concentrations of alcohols.

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Alcohol was obeyed Temkin adsorption isotherm. As an example was given Fig 4. Alcohols were obeyed Temkin adsorption isotherm

Corrosion characteristics of pure Al, Zn, Mg and Cu metals in 1 N  $H_2SO_4$  solutions absence and presence 20 mM alcohols were given Tables 6.

AAS The amounts of elements (Cu, Al, Zn, Mg, Fe, Mn as ppm) were given solutions in  $1 \text{ N H}_2\text{SO}_4$  solution and in  $1 \text{ N H}_2\text{SO}_4 + 20 \text{ mM } 3$ -methyl-1-pentyn-3-ol were shown in Table 7.

### DISCUSSION

Acetylenic alcohols were known as effective corrosion inhibitors of metals in acid media rather than neutrals and alkali media [6, 7]. Organic inhibitors inhibit the corrosion by adsorption at the metal-solution interface or formation of an insoluble metal complex. The inhibition of alcohol on the metal surface was based on the adsorption of alcohol via  $\pi$  electrons of the triple bond rather than the formation of polymer film on the surface [8]. If the polymer film was determined uniform it was closed all of surface. 2-methyl-3-butyn-2-ol and 3-methyl-1-pentyn-3-ol acetylenic alcohol function chemisorptions achieved by the sharing of  $\pi$  electrons in the C=C triple bond with d orbitals of the metal. The molecule is likely to be reduced (electro sorption) via the triple bond on the surface. Subsequent reactions can occur lead to the formation of a protective layer on the anodic zones of the metal. In addition to alcohols in

Table 2. The EDS analysis results of Al alloys

	The form	The forming of intermetallic compounds								
	matrix	white phase	light grey phase							
E-110	Al	Al <sub>2</sub> Si <sub>2</sub> Cu	_							
E-140	Al	Al <sub>13</sub> Fe <sub>1,5</sub> SiCu	AlSi							
E-150	Al	Al <sub>3</sub> Cu <sub>2</sub>	_							
E-160	Al	Al <sub>3</sub> Cu <sub>2</sub>	_							
E-171	Al	Al <sub>5</sub> FeSiMn	_							
E-195	Al	Al <sub>5</sub> FeNi <sub>3</sub>	Si <sub>15</sub> Al							

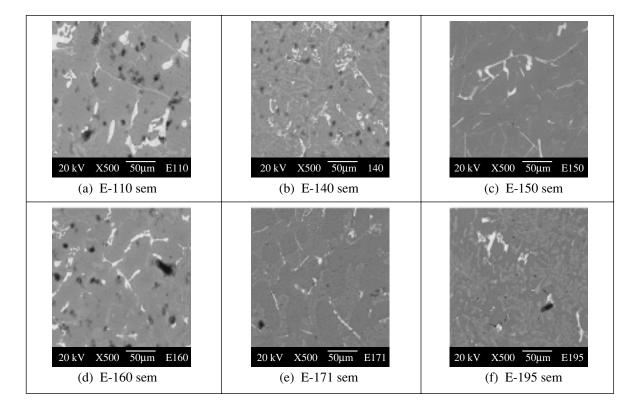


Fig. 1. The SEM microfotograph of alloys (a) E–110, (b) E–140, (c) E–150, (d) E–160, (e) E–171, (f) E–195.

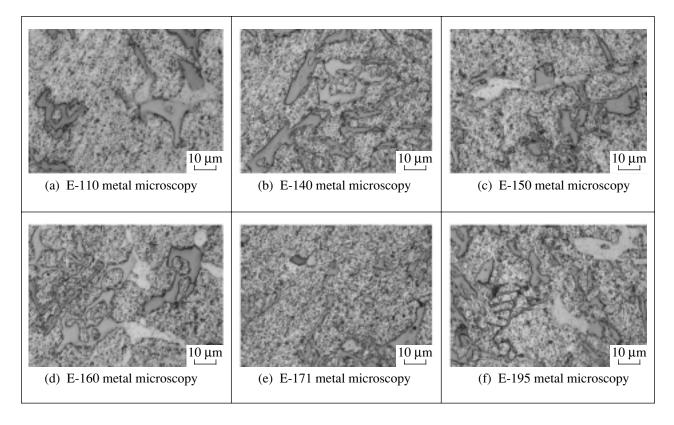


Fig. 2. The metal microscopy microfotograph of alloys 500x (a) E-110, (b) E-140, (c) E-150, (d) E-160, (e) E-171, (f) E-195.

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		E	110			E	140	
Medium	-E <sub>cor</sub> (mV)	$\begin{array}{c} R_p \\ (\Omega \ cm^2) \end{array}$	i <sub>cor</sub> (mA/cm <sup>2</sup> )	% inh. (θ)	-E <sub>cor</sub> (mV)	$\begin{array}{c} R_p \\ (\Omega \ cm^2) \end{array}$	i <sub>cor</sub> (mA/cm <sup>2</sup> )	% inh. (θ)
H <sub>2</sub> SO <sub>4</sub>	600	4.70	10.00		620	17	2.50	
+0.2 mM 1buten3ol	605	47.00	1.00	90	620	43	1.00	60
+1 mM 1buten3ol	605	70.00	0.79	92	625	65	0.80	68
+2 mM 1buten3ol	610	80.00	0.63	94	625	75	0.63	75
+20 Mm 1buten3ol	610	125.00	0.50	95	630	211	0.25	90
+0.2 mM 2methyl3butyn2ol	620	14.50	6.00	40	640	74	0.63	75
+1 mM 2methyl 3 butyn2ol	627	16.00	5.00	50	645	87.8	0.50	80
+2 mM 2methyl 3 butyn2ol	635	18.50	4.00	60	650	108	0.40	84
+20 mM 2methyl 3 butyn2ol	630	44.04	1.26	87	665	385	0.10	96
+0.2 mM 3methyl 2buten1ol	605	15.28	3.16	68	640	23	23	20
+1 mM 3methyl 2 buten 10l	605	17.33	2.50	75	645	35	35	36
+2 mM 3methyl 2 buten 10l	610	41.50	2.00	80	645	41	41	50
+20 mM 3 methyl 12 buten 10l	615	164.00	0.25	97	650	84	84	75
+0.2 mM 3 methyl 3buten10l	610	7.29	8.00	20	640	46	1.00	60
+1 mM 3methyl 3buten1ol	615	10.20	6.31	37	642	55	0.80	68
+2 mM 3methyl 3buten1ol	620	10.40	5.00	50	645	69	0.63	75
+20 mM 3methyl 3buten1ol	630	80.00	0.63	94	650	292	0.20	92
+0.2 mM 3methyl1pentyn3ol	640	10.00	6.00	40	650	63	0.63	75
+1 mM 3methyl1 pentyn3ol	645	11.50	5.00	50	660	150	0.40	84
+2 mM 3methyl1 pentyn3ol	645	19.00	3.98	60	670	234	0.32	87
+20 mM 3methyl1 pentyn3ol	670	74.00	1.00	90	700	438	0.16	94
+0.2 mM 5hexen1ol	610	21.00	2.00	80	620	50	1.00	60
+1 mM 5hexen1ol	612	25.68	1.50	85	622	78	0.65	74
+2 mM 5hexen1ol	615	52.00	1.00	90	625	93	0.40	84
+20 mM 5hexen1ol	630	245.00	0.23	98	630	287	0.20	92

**Table 3.** The corrosion characteristics of E 110 and E 140 alloys 1 N  $H_2SO_4$  and 1 N  $H_2SO_4 + x$  mM alcohol

 $1 \text{ N H}_2\text{SO}_4$  solution the corrosion potentials was shifted more negative values. Alcohol act as indicating a preferential cathodic inhibitor. This results was corrected the idea that alcohol act as cathodic inhibitors in acid media [6, 7].

The thickness of oxide layers on surface of metal was increased important degrees in the solutions containing sulphate anions [9, 10, 11]. The obtained corrosion characteristics for Al-Cu-Si alloys in 1 N H<sub>2</sub>SO<sub>4</sub> and 1 N  $H_2SO_4 + x$  mM alcohol solutions were given Tables 3–5. As can be seen these tables presence protective film on surface of Al alloys have continued. This situation was confirmed the small corrosion currents and high polarization resistance. The increase inhibition efficiency of oxide film was because of insolubility of sulphate salts on metal surface. When the concentration of inhibitor increases the inhibition efficiency and surface coverage degree increases and shift the corrosion potentials in the negative direction [1]. The concentration of 20 mM alcohols were achieved 90% inhibition, which is a rather high.

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The previous results indicated that the application of an anodic potential to aluminum alloy immersed in acid causes oxide film growth. In solutions such as chromic

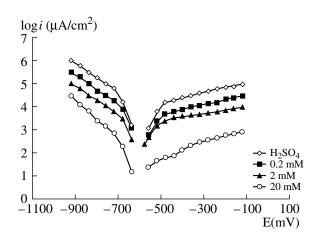


Fig. 3. The potentiodynamic polarization curves for E–150 alloy 1 N  $H_2SO_4$  and 1 N  $H_2SO_4 + x$  mM 1-buten–3-ol.

Table 4. The corrosion characteristics of E150 and E 160 alloys 1 N  $H_2SO_4$  and 1 N  $H_2SO_4 + x$  mM alcohol

		E	150		E 160			
Medium	-E <sub>cor</sub> (mV)	$\begin{array}{c c} R_p \\ (\Omega \ cm^2) \end{array}$	i <sub>cor</sub> (mA/cm <sup>2</sup> )	% inh. (θ)	-E <sub>cor</sub> (mV)	$\begin{array}{c} R_p \\ (\Omega \text{ cm}^2) \end{array}$	i <sub>cor</sub> (mA/cm <sup>2</sup> )	% inh. (θ)
H <sub>2</sub> SO <sub>4</sub>	600	5.50	10.00		600	12.3	4.00	
+0.2 mM 1buten3ol	605	15.30	3.20	68	600	44	1.00	75
+1 mM 1buten3ol	607	21.74	2.20	78	605	85	0.64	84
+2 mM 1buten3ol	615	34.00	1.60	84	605	97	0.40	90
+20 Mm 1buten3ol	610	40.00	0.08	99	610	290	0.16	96
+0.2 mM 2methyl3butyn2ol	605	32.00	2.00	80	645	23	3.20	20
+1 mM 2methyl 3 butyn2ol	610	39.00	1.40	86	650	26	2.80	30
+2 mM 2methyl 3 butyn2ol	615	82.50	1.00	90	654	28.38	2.50	37
+20 mM 2methyl 3 butyn2ol	615	102.00	0.50	95	670	58	1.60	60
+0.2 mM 3methyl 2buten1ol	610	26.00	1.60	84	610	37	1.00	75
+1 mM 3methyl 2 buten 10l	612	50.00	1.00	90	612	83	0.56	86
+2 mM 3methyl 2 buten 10l	615	79.00	0.63	94	615	140	0.32	92
+20 mM 3 methyl 12 buten 10l	620	161.00	0.28	97	625	185	0.20	95
+0.2 mM 3 methyl 3buten1ol	605	12.90	3.80	62	605	24	2.50	37
+1 mM 3methyl 3buten1ol	607	19.00	3.16	68	605	34	1.6	60
+2 mM 3methyl 3buten1ol	610	29.00	2.50	75	605	45	1.00	75
+20 mM 3methyl 3buten1ol	620	32.00	2.00	80	610	63	0.80	80
+0.2 mM 3methyl1pentyn3ol	620	11.60	4.00	60	620	19	2.50	37
+1 mM 3methyl1 pentyn3ol	625	22.00	2.50	75	625	36	1.60	60
+2 mM 3methyl1 pentyn3ol	630	36.00	2.20	78	630	62	1.00	75
+20 mM 3methyl1 pentyn3ol	640	62.00	0.80	92	664	309	0.16	96
+0.2 mM 5hexen1ol	610	18.00	2.50	75	610	53	1.00	75
+1 mM 5hexen1ol	612	60.00	1.00	90	612	84	0.63	84
+2 mM 5hexen1ol	615	87.00	0.63	94	615	118	0.32	92
+20 mM 5hexen1ol	620	244.00	0.20	98	625	257	0.25	94

and sulfuric acids, the oxide film is characterized by a duplex structure composed of a thin barrier layer under a thick porous layer [12]. An anodic film on the Al surface consists of barrier and porous layers and the formation of the anodic film consist of three steps i.e. the formation of the barrier layer, the formation and development of the porous film. The barrier type film is compact, thin and free of pores. It is known that the barrier layer is an electric insulator and the growth of the subsequent porous film depends on the immigration of the cations and anions (e.g. O<sup>2-</sup>, OH<sup>-</sup>, Al<sup>3+</sup>) through the barrier layer in order to form a film at the oxide/substrate interface [13, 14, 15]. Adsorption of alcohols on the Al surface probably closed the porosities and this decreased the corrosion. This closing effect is related to structure of alcohols. If alcohols were smaller they were closed anodic zones on top of surface of alloy and the corrosion were decreased.

Copper is one of the most important alloying elements due to its appreciable strengthening effect. Alloys containing different elements lead to the presence of several intermetallic phases. An SEM micrograph of the alloys surface is presented Figure II and allows to identify these different phases. This suggests that anodic particles are dissolved preferentially and cathodic particles promote dissolution on the neighboring matrix [12, 16] The microstructure of this alloy consists of primary silicon and Al–Si eutectic under normal cast condition [17]. Near eutectic Al–Si alloys exhibits complex multiphase microstructures, comprising primary (blocky) and eutectic (acicular) Si, Al dendrites and numerous intermetallic particles [16].

On the other hand surface of alloys were different rather than pure Al. At this condition may be partial change. For example if amount of copper were too much and alcohols were adsorptioned on surface of Cu,

		E	171			E	195	
Medium	-E <sub>cor</sub> (mV)	$\begin{array}{c c} R_p \\ (\Omega \ cm^2) \end{array}$	i <sub>cor</sub> (mA/cm <sup>2</sup> )	% inh. (θ)	-E <sub>cor</sub> (mV)	$\begin{array}{c} R_p \\ (\Omega \ cm^2) \end{array}$	i <sub>cor</sub> (mA/cm <sup>2</sup> )	% inh. (θ)
H <sub>2</sub> SO <sub>4</sub>	610	19.48	3.20		580	13.30	5.60	
+0.2 mM 1buten3ol	645	118	0.50	84	585	197.00	0.32	94
+1 mM 1buten3ol	650	170	0.40	87	587	250.00	0.25	95
+2 mM 1buten3ol	655	198	0.32	90	590	494.00	0.20	96
+20 Mm 1buten3ol	685	358	0.16	95	595	981.00	0.126	98
+0.2 mM 2methyl3butyn2ol	630	76	1.00	69	600	47	1.00	82
+1 mM 2methyl 3 butyn2ol	635	165	0.41	87	605	89	0.50	91
+2 mM 2methyl 3 butyn2ol	640	266	0.25	92	610	168	0.30	95
+20 mM 2methyl 3 butyn2ol	645	1152	0.05	98	615	309	0.20	96
+0.2 mM 3methyl 2buten1ol	640	39	1.26	61	585	75	0.63	89
+1 mM 3methyl 2 buten 10l	650	65	0.70	78	590	103	0.45	92
+2 mM 3methyl 2 buten 1ol	660	104	0.56	82	590	172	0.32	94
+20 mM 3 methyl 12 buten 10l	700	340	0.16	95	600	326	0.16	97
+0.2 mM 3 methyl 3buten1ol	620	41	1.00	69	590	90	0.40	93
+1 mM 3methyl 3buten1ol	625	106	0.56	82	590	170	0.30	95
+2 mM 3methyl 3buten1ol	630	128	0.40	87	590	193	0.25	95
+20 mM 3methyl 3buten1ol	640	362	0.16	95	595	423	0.16	97
+0.2 mM 3methyl1pentyn3ol	650	54	1.00	69	590	88.50	0.63	89
+1 mM 3methyl1 pentyn3ol	660	96	0.67	79	595	177	0.40	93
+2 mM 3methyl1 pentyn3ol	670	152	0.40	87	600	251	0.25	95
+20 mM 3methyl1 pentyn3ol	685	347	0.18	94	610	364	0.12	98
+0.2 mM 5hexen1ol	640	91	0.63	80	590	44	1.00	82
+1 mM 5hexen1ol	645	112	0.50	84	595	77	0.63	89
+2 mM 5hexen1ol	650	134	0.40	87	600	179	0.25	95
+20 mM 5hexen1ol	700	340	0.16	95	610	280	0.20	96

Table 5. The corrosion characteristics of E 171 and E 195 alloys 1 N  $H_2SO_4$  and 1 N  $H_2SO_4 + x$  mM alcohol

which is related to interaction and adsorption on the surface of Cu. If the majority of surface is Al inhibition effect increase. It was seen that SEM micrograph if the alloys of matrix rich of Al small molecules of alcohol is much more effective (like as E110, E195 and E171). The results of to obtain by Polat in NaOH +  $Na_2SO_4$ , NaOH and Na<sub>2</sub>SO<sub>4</sub> solutions the inhibition effect of sulphate ions were clearly showed. This effect of sulphate ions in film of oxide/hydroxide can be seen on the surface of Al. Some previous workers [8, 19, 20, 21, 22, 23, 24] stated that sulphate ions acted as inhibitor. If concentration is high enough for formation of 1 Al(OH)SO<sub>4</sub> this stuation passivates the surface of Al [24]. It can be seen that this study inhibition percentage efficiency more Al alloys were revealed high values. Experimental results corrected with previous works [8, 21, 25].

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Oxide film on Al surface have two evident layers an out layer-rich Al ions of electrolyte and inside surface to be formation of pure Al oxide the media of containing anion ions [21]. In addition the concentration of 20 mM alcohol in 1 N H<sub>2</sub>SO<sub>4</sub> was seen structure of doublex film on Al surface. This oxide were obtained Faraday's law interface of metal/oxide [14]. Look at the corrosion of pure metals @ in 1 N H<sub>2</sub>SO<sub>4</sub> solution and addition 20 mM alcohols this solution (Table 6) at the corrosion of pure zinc the most effect alcohol is 3-methyl-1-pentyn-3-ol as for the corrosion of pure Al the most effect alcohols are 1-buten-3-ol and 2-methyl-3-butyn-2-ol. Small alcohols were more effected. This aforementioned for H<sub>2</sub>SO<sub>4</sub> solution were suitable think of the closed porous on top of surface. The corrosion of pure copper almost all of alcohol were more inhibited this state. In that case the increase of amount copper on surface of alloys were

		pure	e Mg		pure Zn				
Medium	-E <sub>cor</sub> (mV)	$R_p$ ( $\Omega \ cm^2$ )	i <sub>cor</sub> (mA/cm <sup>2</sup> )	% inh. (θ)	-E <sub>cor</sub> (mV)	$\begin{array}{c} R_p \\ (\Omega \ cm^2) \end{array}$	i <sub>cor</sub> (mA/cm <sup>2</sup> )	% inh. (θ)	
H <sub>2</sub> SO <sub>4</sub>	1980	1.58	100		1080	0.84	135		
1buten3ol	1992	4.0	32	68	1100	1.29	56	58	
2methyl3butyn2ol	2000	3.8	36	64	1110	3.26	45	67	
3methyl2buten 1ol	2000	3.3	40	60	1090	1.71	89	34	
3methyl3buten1ol	1995	4.0	40	60	1130	1.00	40	70	
3methyl1pentyn3ol	2010	4.5	35	65	1120	4.80	10	92	
5hexen1ol	2000	3.1	32	68	1095	1.55	100	26	
		pure	e Al		pure Cu				
	-E <sub>cor</sub> (mV)	$\begin{array}{c} R_p \\ (\Omega \ cm^2) \end{array}$	i <sub>cor</sub> (mA/cm <sup>2</sup> )	% inh. (θ)	-E <sub>cor</sub> (mV)	$\begin{array}{c} R_p \\ (\Omega \ cm^2) \end{array}$	i <sub>cor</sub> (mA/cm <sup>2</sup> )	% inh. (θ)	
H <sub>2</sub> SO <sub>4</sub>	810	100	0.631		200	100	1		
1buten3ol	820	1543	0.045	93	210	180	0.5	50	
2methyl3butyn2ol	850	765	0.079	87	230	890	0.032	97	
3methyl2buten 1ol	820	430	0.200	68	225	2000	0.010	99	
3methyl3buten1ol	820	232	0.316	50	235	1500	0.025	97.5	
3methyl1pentyn3ol	850	543	0.158	75	260	1600	0.010	99	
5hexen1ol	830	172	0.320	49	250	650	0.200	80	

Table 6. The corrosion characteristics of pure Mg, Zn, Al and Cu 1 N  $H_2SO_4$  and 1 N  $H_2SO_4$  + 20 mM alcohol

**Table 7.** The values of elements (ppm) in 1 N  $H_2SO_4$  solution and 1 N  $H_2SO_4$  + 20 mM 3metil1pentin3ol solution

		$1 \text{ N H}_2 \text{SO}_4 \text{ solution}$								
Alloys	Al	Cu	Fe	Mg	Mn	Zn				
E110	2.79	0.03	0.15	0.02	0.03	0.39				
E140	2.67	0.01	0.23	0.02	0.04	0.20				
E150	5.34	0.06	0.77	0.05	0.04	0.24				
E160	2.40	0.02	0.21	0.01	0.02	0.14				
E171	5.65	0.01	0.24	0.15	0.09	0.09				
E195	4.89	0.01	0.22	0.61	0.01	0.19				
		1 N H	$I_2 SO_4 + 20 \text{ mM } 31$	netil1pentin3ol so	lution					
	Al	Cu	Fe	Mg	Mn	Zn				
E110	1.69	0.02	0.18	0.00	0.04	0.24				
E140	1.74	0.08	0.61	0.15	0.04	1.18				
E150	1.91	0.01	0.54	1.93	0.09	8.91				
E160	10.18	0.02	0.99	0.99	0.16	4.84				
E171	2.69	0.33	0.68	0.09	0.04	15.65				
E195	3.94	0.05	0.21	0.39	0.00	0.16				

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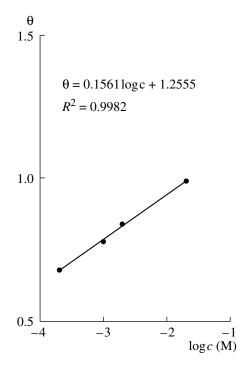


Fig. 4.  $\theta$ -logC plot 1-buten-3-ol in 1 N H<sub>2</sub>SO<sub>4</sub> for E-150 alloy. M)

revealed increase inhibition efficiency. If copper have hadn't left formation on intermetallics compounds it would have been scattered regularly on the surface. The corrosion was decreased (inhibition efficiency were increased). Just as E171 and E195 alloys were increased the efficiency of inhibition. Because of amount of Cu on the surface of alloy was caused inhibition increase. In the even that the percent of aluminum was gone into solution was too more. Al on top of surface of alloys was decreased (Table 7). Media of 20 mM concentration of inhibitor the most amount of Al were gone into solution at the E160 alloy. The inhibition were least this alloy (Table 4) this that aforementioned was suitable. But at this alloy the highest amount of Cu concentration, this bad effect were partial decreased. Also partial if the little amount of Al passed solution (Table 7) as like E195 alloy the best inhibition would achieve. Because of that also conclusions were possible if region of matrix on surface of alloys increase inhibition efficiency will increase. Just as at the amount of the region of matrix as E195, E171, E110 alloys, percent inhibition could be high (Tables 3–5)

The results of EDS of alloys were revealed different intermetallic compounds on surface of alloys (Table 2). This were changed structure of alloy surface and the activity of alcohols. From the percent atom values, the formation of intermetallic compounds were given Table 2. It can be seen from Table 2 matrix has had only Al (other elements were impurity), white phase and lightly phase from one alloy to another alloy have had a different

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structure. Some alloys has had lightly gray phase a little rather than other alloys. One another observation if the corrosion potential of alloy more than positive inhibition efficiency will have bigger. The results of structure of  $OH^-$  was opened up H<sup>+</sup> structure of negative charge was too many adsorplaned on surface of positive electrode. Because of the positive electrode potentials were more shifted positive values. The inhibition action of alcohols were increased in that corrosion potentials of pure Cu and pure Al were shifted more positive values rather than other pure Zn and Mg. As a result contribution inhibition activity of alcohols (Table 6) were increased. When formation of free (Mg and Zn) structure of alloys are given to solution alloys will rich Cu and Al and inhibition efficiency was increased.

Adsorption of alcohols on surface of alloys were obeyed Temkin adsorption's isotherm. This also alcohols were closed active zones on the surface of alloy [1, 26, 27].

#### CONCLUSIONS

On the surface of Al and its alloys in 1 N  $H_2SO_4$  solution were had both barrier layer and porous layer.

The studied alcohols in  $1 \text{ N H}_2\text{SO}_4$  solution for pure Al and pure Cu were efficiency inhibitor.

Aforementioned alcohols in  $1 \text{ N H}_2\text{SO}_4$  solution for Al-Cu-Si alloys have been behavior as cathodic inhibitor.

The effect of alcohols were related to porous and barrier layer on surface of alloys were shown differently. On the porous layer small molecule's alcohols were actived, on the barrier layers big molecules of alcohols were actived.

Adsorption of alcohols on the surface of alloys were shown differently related to structure of surface of alcohols and alloys. The best adsorption have been structure of porous oxide layer.

Adsorption of alcohols on surface of alloys were obeyed Temkin adsorption's isotherm.

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#### REFERENCES

- 1. Sahin, M. and Bilgic, S., *Appl. Surf. Sci.*, 1999, vol. 147, p. 27.
- Patermarakis, G., Moussoutzanis, K., *Corros. Sci.*, 2002, vol. 44, p. 1737.
- Badawy, W.A. and Al-Kharafi, F.M., *Corros. Sci.*, 1997, vol. 39, p. 681.
- 4. Al-Kharafi, F.M. and Badawy, W.A., *Electrochimica* Acta, 1995, vol. 40, p. 1811.

- 5. Di Li, Yangling Hu, Baolan Guo, *Mate.Sci. and Engineering*, 2000, vol. 280, p. 173.
- 6. Tedeshi, R.J., Corrosion, 1975, vol. 31, pp. 130.
- Fiaud, C., Harch, A., Mallouh, D., and Tzinmann, M., *Corros. Sci.*, 1993, vol. 35, p. 1437.
- Aksut, A.A. and Onal, A.N., *Corros. Sci.*, 1997, vol. 39, pp. 761.
- Shimizu, K., Kobayashi, K., Thomson, G.E., et. al., Corros. Sci., 1997, vol. 39, p. 281.
- 10. Crossland, A.C., Thomson, G.E., Smith, C.J.E., et. al., *Corros. Sci.*, 1999, vol. 41, p. 2053.
- 11. Zhou, X., Shimizu, K., Thomson, G.E., et. al., *Corros. Sci.*, 1999, vol. 41, p. 1599.
- 12. Moutarlier, V., Gigandet, M.P., Papetti, J., Normand, B., Surface and Coating Technology, 2002, vol. 161, p. 267.
- 13. Habazaki, H., Paez, M.A., Zhou, X., et. al., *Corros. Sci.*, 1996, vol. 38, p. 1033.
- 14. Paez, M.A., Foong, T.M., Ni, C.T., et. al., *Corros.Sci.*, 1996, vol. 38, p. 59.
- 15. Zhang, Q. and Wang, W., *Mater. Sci. and Engineering*, 2000, vol. 280, p. 168.
- 16. Mazhar, A.A., Arab, S.T., and Noor, E.A., *J. Appl. Electrochem.*, 2001, vol. 31, p. 1131.

- 17. Zhang, R., Cao, Q., Pang, S., et. al., *Science and Technology of Advanced Materials*. 2, 2001, vol. 3.
- Polat, R., Anodic Oxide Films Formed on Aluminium Surfaces in Different Electrolytes, *Ph.D. Thesis*, Ankara, 1997, p. 306
- 19. Funkhouser, J.G., Corrosion., 1961, vol. 17, p. 109.
- 20. Aksut, A.A., Electrochemica Acta, 1983. vol. 28, p. 1177.
- 21. Bockris, J.O'M. and Yang, B., *Electrochemica Acta*, 1991a, vol. 36, p. 1333.
- 22. Cabot, P.L., Centellas, F.A., Perez, E., and Loukili, R., *Electrochemica Acta*, vol. 38, p. 2741.
- 23. Aksut, A.A. and Bayramoglu, G., *Corros. Sci.*, 1994, vol. 36, p. 415.
- 24. Frigrani, A. and Trabanelli, R., *Corrosion*, 1999, vol. 55, p. 653.
- 25. Bockris, J.O'M. and Yang, B., J. Electrochemical Society, 1991b, vol. 138, p. 2237.
- Skeldon, P., Shimizu, K., Thomson, G.E., and Wood, G.C., *Thin Solid Films*, 1985, vol. 123, p. 127.
- Bilgic, S. and Sahin, M., *Appl. Surf. Sci.*, 1999b, vol. 70, p. 290.

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