

## EFFECT OF THE ANODIZATION CURRENT DENSITY AND TIME ON THE CORROSION OF Al AND Al-Mn ALLOY

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Al and Al Mn alloy were anodized in 1.0 M solution of sulphuric, oxalic, citric and tartaric acids at various current densities (0.5-2.50 a.dm<sup>-2</sup>). It is found that the inhibition property of the anodic films on both Al and Al-Mn increased with increasing the current density. The effect of current density is greater in case of citric and tartaric acids. The effect of time was studied in 1.0 M acid solution at 1.0 a.dm<sup>-2</sup> and time intervals of 10-60 minutes. Increasing the time accompanied with a decrease in reaction number. The results were treated applying both of Mylius equations and the mathematical treatment suggested earlier by us.

*Key words* Corrosion, Al-Mn alloy, Anodization, Aluminium.

### INTRODUCTION

The effect of current density and time on the rate of corrosion of Al and its alloys Al-Mn, Al-Mg, Al-Zn and Al-Cu was the subject of many investigations.

The anodization of Al-5.0 % Mg and Al-2.0 % Zn was studied [1] in 1.5 M H<sub>2</sub>SO<sub>4</sub> at 20° for one hour at 250 a.m<sup>-2</sup>. The films formed have thickness up to 50 nm and incorporated by Mg and Zn to approximately their alloying proportions. The same behaviour was reported for Al-4.0 % Cu. Keller and Edwards [2] claimed that CuAl<sub>2</sub> oxidizes or dissolves faster than aluminium but Koch [3] considered that CuAl<sub>2</sub> can be anodized.

The specific resistance of the initial anodic films formed on pure aluminium at 50-6000 a.m<sup>-2</sup> was studied [4] in a range of aliphatic and aromatic acids up to 1.0 M at 25°. The acids were with and without -OH, -NH<sub>2</sub>, -CH<sub>3</sub>, -C<sub>6</sub>H<sub>5</sub>, -Cl substituents and unsaturated bonds. It is concluded [4] that depending on the acid type, concentration and temperature and the filming current density, monocarbonic and chlorine containing acids yield anodic pitting and corrosion in very thin initial barrier type layers. Kape [5] presented voltage-time curves at constant current density for a range of acids. Strong anodizing acids such as sulphuric and sulfonic work at nearly constant voltage at room temperature and produce nearly clear films of natural colour. Weak anodizing acids like tartaric, malonic and sulfosalicylic tend to have a rising voltage-time curve and produce dark films.

In the present work, the effect of anodization current density and time on the corrosion resistance of Al and

Al-Mn was studied in sulphuric, oxalic, citric and tartaric acids.

### EXPERIMENTAL

The specimens of Al and Al-Mn sheets (100 x 10 mm) were degreased [6] in a solution of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>3</sub>PO<sub>4</sub> at 85° for 5 minutes. The percentage chemical composition of Al is Mn, 0.10, Si; 0.10 and Fe, 0.10 and for Al-Mn is Mn; 2.0, Si; 0.10 and Fe; 0.10. The anodization of specimens was carried out in a cell of size 200 x 100 mm in dimensions containing 250 ml of anodizing solution.

The effect of the applied current densities 0.50, 1.00, 1.50 and 2.50 a.dm<sup>-2</sup> in presence of 1.0 M of anodizing acids sulphuric, oxalic, citric and tartaric at 30° for 60 minutes was studied.

The effect of anodization time 10, 20, 30, 40, 50 and 60 minutes at acid concentration 1.0 M and current density 1.0 a.dm<sup>-2</sup> was also investigated. The anodized specimens were dipped in 30 ml of 3.0 N HCl at 30° placed in Mylius apparatus [7]. The rise of temperature with time was followed using a 100° thermometer. All experiments were carried out in adiabatic conditions as the apparatus was kept in a Dewar flask which is fixed in an air thermostat at 30°

### RESULTS AND DISCUSSION

The effect of the anodization current density (0.5-2.5 a.dm<sup>-2</sup>) on the corrosion resistance of Al and Al-Mn alloy was studied in presence of 1.0 M of the anodizing acid. The anodization time was 60 minutes for sulphuric and oxalic acids and 5 minutes for citric and tartaric acids. The values of reaction number and inhibition which were calculated using Mylius [7] equations are given in

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Table 1. Generally it is obvious that with increasing the anodization current density, the reaction number decreased and the corrosion resistance of the formed anodic film increased. However, the effect of current density is greater

Table 1. (R.N.) and A(in brackets) values for Al and Al-Mn anodized for one hour in 1.0 M H<sub>2</sub>SO<sub>4</sub> and oxalic acids and for 5.0 minutes in citric and tartaric acids at different current densities.

Current density a dm <sup>-2</sup>	H <sub>2</sub> SO <sub>4</sub>		Oxalic acid		Citric acid		Tartaric acid	
	Al	Al-Mn	Al	Al-Mn	Al	Al-Mn	Al	Al-Mn
0.0	2.63	7.56	2.63	7.56	2.63	7.56	2.63	7.56
0.5	0.75 (71.5)	1.74 (76.9)	0.87 (67.1)	1.23 (83.8)	0.92 (65.4)	1.9 (75.1)	0.92 (65.4)	1.9 (75.1)
1.0	0.80 (69.9)	1.71 (77.4)	0.73 (72.5)	1.23 (83.8)	1.02 (61.6)	1.64 (78.2)	1.02 (61.6)	1.64 (78.2)
1.5	0.76 (71.2)	1.32 (82.5)	0.68 (74.2)	1.20 (84.0)	1.23 (53.7)	1.63 (78.6)	1.23 (53.7)	1.63 (78.6)
2.5		1.30 (82.8)	0.64 (75.9)	1.17 (84.5)	0.53 (80.1)	1.29 (82.9)	0.53 (80.1)	1.29 (82.9)

in the case of citric and tartaric acids. The change in corrosion resistance with oxalic and sulphuric acids is small. These observations may be due to the variation in the film thickness. In oxalic and sulphuric acids, the anodic film is of porous type, since the voltage drop across the anodization cell does not vary very much with time. Consequently, the increase in current density may lead to the formation of a greater number of pores on unit surface area together with greater thickness of the film [8]. In citric and tartaric acids the observed high effect may be attributed to the film packing, its cohesion and compactness.

The relation  $\log \Delta T - t$  for the dissolution of anodized Al and Al-Mn in 1.0 M sulphuric acid at different current densities is shown in Fig. 1 as representative results. The constants a and b of the empirical equation [9]  $t = a + b \log \Delta T$  were evaluated from which the relative decrease in

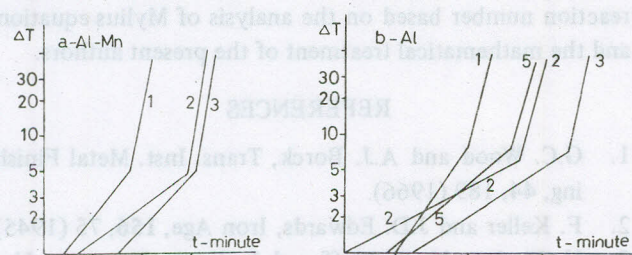


Fig. 1. Log  $\Delta T - t$  curves for (a) Al-Mn: 1, 2-1.5 and 3-2.50 a.dm<sup>-2</sup> (b) Al: 1-0.25, 2-0.50, 3-0.75, 4-1.0 and 5-1.50 a.dm<sup>-2</sup> anodized in 1.0 M sulphuric acid at 30°

the corrosion rate (A) was calculated at different temperatures (Tables 2 and 3). The symbol A<sub>1</sub> is characteristic for the initiations of corrosion at  $\Delta T = 0.5^\circ$ ,  $\Delta T^*$  is the elevation in temperature at the inflection point in the straight line relations  $\log \Delta T - t$  which indicates the transition of the dissolving phase from oxide to metal state, A<sub>2</sub> is the relative decrease in the corrosion at  $\Delta T < \Delta T^*$  and A<sub>3</sub> at  $\Delta T > \Delta T^*$ . A<sub>3</sub> values of the porous type formed in sulphuric and oxalic acids are lower than the barrier type anodic films in citric and tartaric acids. This could be caused by the very resistive barrier films which does not dissolve easily as the porous type. The resistance of the barrier type makes the corrosion start from any defect due to crack on the surface. Thus, at  $\Delta T^*$ , the metal surface is not entirely activated, but may be partially free from the highly resistive barrier film. Therefore, A<sub>3</sub> in citric and tartaric acids is higher than in sulphuric and oxalic acids.

The effect of anodization time (10-60 min.) was studied in 1.0 M acid solution at 30° and 1.0 a.dm<sup>-2</sup>. The results of  $\Delta T - t$  measurements indicated that the

Table 2. a,b Constants and relative decrease in corrosion rate A of Al and Al-Mn anodized in 1.0 M H<sub>2</sub>SO<sub>4</sub> at different current densities.

	C.d. a.dm <sup>-2</sup>	a <sub>1</sub>	b <sub>1</sub>	$\Delta T^*$	b <sub>2</sub>	A <sub>1</sub> %	A <sub>2</sub> %	A <sub>3</sub> %
Al	0.0	11.8	5.0	-	-	-	-	-
	0.5	40.0	45.0	36.0	6.5	70.5	88.9	23.08
	1.0	64.5	9.0	38.5	6.0	81.7	44.4	16.7
	1.5	48.5	28.0	37.8	6.7	75.67	82.14	25.92
Al-Mn	0.0	2.6	2.0	-	-	-	-	-
	0.5	19.0	20.0	35.0	4.5	86.3	90.0	55.56
	1.0	20.5	17.25	36.0	4.2	92.2	88.41	52.38
	1.5	22.0	33.5	34.8	3.5	88.1	94.03	42.86
2.5	30.75	22.75	35.0	3.5	91.4	91.21	42.86	

Table 3. a,b Constants and relative decrease in corrosion rate A of Al and Al-Mn anodized in 1.0 M oxalic acid at different current densities.

	C.d. a.dm <sup>-2</sup>	a <sub>1</sub>	b <sub>1</sub>	$\Delta T^*$	b <sub>2</sub>	A <sub>1</sub> %	A <sub>2</sub> %	A <sub>3</sub> %
Al	0.0	11.8	5.0	-	-	-	-	-
	0.5	37.5	24.0	35.5	8.0	68.53	79.2	37.5
	1.0	38.5	38.0	37.0	6.5	69.4	86.8	23.1
	1.5	41.5	44.0	35.2	8.0	71.57	88.64	37.5
2.5	35.5	56.5	36.8	8.0	66.76	91.20	37.5	
Al-Mn	0.0	2.6	2.0	-	-	-	-	-
	0.5	25.5	23.5	36.5	5.5	89.8	91.41	63.64
	1.0	25.0	24.0	39.0	7.0	89.6	91.67	71.43
	1.5	19.5	32.25	37.4	5.5	86.7	93.8	63.64
2.5	16.25	35.0	37.8	5.5	84.0	94.3	63.64	

increase in anodization time leads to a decrease in the reaction number and an increase in the corrosion resistance. Table 4 is taken as a representative data for Al and Al-Mn anodized in sulphuric and oxalic acids. The results of  $t_{1/2}$  (time intervals at which  $T = \Delta T_m/2$ ) are reported in Table 5 which indicate that  $t_{1/2}$  increase with increasing the anodization time in case of sulphuric and oxalic acids, but with citric and tartaric acids an irregular values of  $t_{1/2}$  were obtained. These may be due to the difference in the nature of the film thickness formed.

Table 4. R.N. and A (in brackets) values for Al and Al-Mn anodized for time intervals in 1.0 M H<sub>2</sub>SO<sub>4</sub> and oxalic acids.

Time of anodization, minutes	H <sub>2</sub> SO <sub>4</sub>		Oxalic acid	
	Al	Al-Mn	Al	Al-Mn
0.0	2.63	7.56	2.63	7.56
10.0	1.13 (57.3)	2.09 (72.3)	0.97 (63.4)	1.79 (76.3)
20.0	1.07 (59.5)	1.84 (75.7)	1.08 (59.1)	1.66 (78.0)
30.0	1.04 (60.9)	1.78 (76.5)	1.08 (59.4)	1.64 (78.3)
40.0	0.97 (63.4)	1.84 (75.7)	1.30 (51.1)	1.58 (79.1)
50.0	0.88 (66.7)	1.94 (74.3)	0.89 (66.3)	1.53 (79.8)
60.0	0.80 (71.2)	1.30 (82.8)	0.73 (72.5)	1.23 (83.7)

Table 5.  $t_{1/2}$ , minutes for Al and Al-Mn anodized in 1.0 M of acid at 1.0 a.dm<sup>-2</sup> for time intervals.

Time of anodization minutes	H <sub>2</sub> SO <sub>4</sub>		Oxalic		Citric		Tartaric	
	Al	Al-Mn	Al	Al-Mn	Al	Al-Mn	Al	Al-Mn
0.00	19.0	6.0	19.0	6.0	19.0	6.0	19.0	6.0
10.0	52.0	29.5	63.0	34.0	54.0	28.0	53.5	33.0
20.0	55.5	34.0	56.0	37.5	64.5	37.0	74.0	49.5
30.0	58.5	35.5	56.0	38.0	70.0	36.0	58.0	53.0
40.0	61.5	35.5	67.5	38.0	85.0	44.5	66.5	50.5
50.0	67.0	-	64.5	41.0	68.0	39.0	70.0	38.0
60.0	76.0	37.0	54.5	51.0	90.5	42.5	64.5	48.0

The results were also treated using the equation  $t = a + b \log \Delta T$  and the values of A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub> and  $\Delta T^*$  were

obtained as given in Table 6 where the anodization is carried out in sulphuric acid. The values of A<sub>1</sub> and A<sub>2</sub> were always close to each other but much higher than A<sub>3</sub>. This is in accordance with the idea that at  $\Delta T K T^*$ , the active metal surface is the phase interacting with the aggressive medium (3.0 N HCl), below  $\Delta T^*$  the anodic film is still existing and thus A<sub>1</sub> and A<sub>2</sub> are of considerable value.

Table 6. a, b Constants and relative decrease in corrosion rate A of Al and Al-Mn anodized in 1.0 M H<sub>2</sub>SO<sub>4</sub> for time intervals.

	Time minutes	a	b <sub>1</sub>	$\Delta T^*$	b <sub>2</sub>	A <sub>1</sub> %	A <sub>2</sub> %	A <sub>3</sub> %
Al	0.0	11.8	5.0	-	-	-	-	-
	10.0	35.0	15.0	37.6	5.0	66.28	66.7	zero
	20.0	39.0	16.0	37.6	5.0	69.74	68.8	zero
	30.0	42.5	13.5	37.8	5.0	72.24	63.0	zero
	40.0	46.5	12.5	37.6	5.0	74.62	60.0	zero
	50.0	54.5	10.0	38.0	5.0	78.35	50.0	zero
	60.0	64.5	9.0	38.5	6.0	81.70	44.4	16.7
Al-Mn	0.0	2.6	2.0	-	-	-	-	-
	10.0	16.0	15.25	35.2	3.0	83.75	86.9	33.33
	20.0	17.0	20.0	34.0	6.0	84.71	90.0	66.67
	50.0	17.5	15.75	35.6	3.0	85.14	87.30	33.33
	60.0	20.5	17.25	36.0	4.2	87.32	88.41	52.38

The dissolution of Al and Al-Mn anodized in citric and tartaric acids gave A<sub>3</sub> of a considerable value. This may be attributed to the basically different type of the anodic film formed in these acids. It seems that the dissolution takes place via a subsurface mechanism, while the anodic film is extremely stable in the aggressive medium. Thus the inflection at  $\Delta T^*$  may be due to the partial and not complete elimination of the anodic film.

## CONCLUSION

The inhibition property of anodic oxide films formed in sulphuric, oxalic, citric and tartaric acids on Al and Al-Mn alloy increased with increasing current density. The effect of current density is greater in the case of citric and tartaric acids. Increasing the anodizing time decreases the reaction number based on the analysis of Mylius equations and the mathematical treatment of the present authors.

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Excess Volumes ( $V^E$ ) and deviations in isentropic compressibilities ( $K$ ) were reported for the binary liquid mixtures of *N,N*-dimethylformamide (DMF) with 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, dichloroethane and tetrachloroethane over the entire mole fraction range at 303.15 K. The values of  $V^E$  and  $K$  are positive for the system, DMF + 1,1,2-trichloroethane and negative for the system, DMF + 1,1,1-trichloroethane and + 1,1,2,2-tetrachloroethane. For DMF + dichloroethane, the values of  $V^E$  are negative and an inversion in sign of  $K$  from positive to negative is observed. The  $V^E$  values for the system, DMF + tetrachloroethane, are negative and  $K$  values are positive. The experimental data were used to explain the effect of successive chlorination and unsaturation of ethane molecule on  $V^E$  and  $K$ .

Key words: Excess volumes, sound velocity, Density.

INTRODUCTION

The present paper forms a part of our programme on the measurement of thermodynamic properties of mixtures containing chlorinated hydrocarbons as one of the components [1-3]. We report here new experimental data on excess volumes and deviations in isentropic compressibilities for the mixtures of DMF with 1,1,2-trichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, dichloroethane and tetrachloroethane at 303.15 K. We have undertaken this work to investigate the effect of successive chlorination and desaturation of ethane molecule on excess volumes and deviations in isentropic compressibilities.

EXPERIMENTAL

Excess Volumes ( $V^E$ ) were measured directly using a single composition per loading type dilatometer described by Rao and Naidu [4]. Five dilatometers with different capacities were used to cover the entire composition range. The values of  $V^E$  are accurate to  $\pm 0.003$  cm<sup>3</sup> mol<sup>-1</sup>. Isentropic compressibilities were calculated from the relation

$$K = U^2 \rho \tag{1}$$

where  $U$  and  $\rho$  denote sound speed and density. Sound speeds in liquids and liquid mixtures were measured with a single crystal ultrasonic interferometer working at a fixed frequency. The densities of the mixtures were computed from experimental excess volume data (Table 1) using the relation

$$\rho = \frac{M_1 x_1 + M_2 x_2}{V^E + V^0} \tag{2}$$

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where  $x_1$  and  $x_2$  denote mole fractions and  $M_1$  and  $M_2$  stand for the molecular weights.  $V^0$  and  $V^E$  represent ideal molar volume and excess molar volume of the mixture. Densities of the pure components were determined using a dilatometer. Deviation in isentropic compressibility was calculated using the relation

$$K = K_1 - \sum x_i K_i \tag{3}$$

where  $K$ ,  $K_1$  and  $K_i$  are the isentropic compressibilities of the mixture and the pure components 1 and 2 respectively.  $\sum x_i$  and  $\sum K_i$  are the volume fractions.  $K$  represents the deviation in isentropic compressibility from the ideal behaviour.  $K$  values are accurate to  $\pm 1.2\%$ .

Materials *N,N*-dimethylformamide (AR) was purified by the method described by Ramapal et al. [5]. 1,1,2,2-tetrachloroethane (BDH), 1,1,1-trichloroethane (Koch-light) and 1,1,2-trichloroethane (BDH) were purified by the methods described by Ramanjaneyulu et al. [3]. Tetrachloroethane (BDH) and trichloroethane (BDH) were purified using the method described by Riddick and Bunger [6]. The measured densities and boiling points of the pure components are in good agreement with the literature values.

RESULTS AND DISCUSSION

Experimental  $V^E$  values for the binary liquid mixtures are included in Table 1. Dependence of  $V^E$  on mole fraction in graphically presented in Fig. 1. The values of density ( $\rho$ ), sound speed ( $U$ ), isentropic compressibility ( $K$ ) and deviation in isentropic compressibility ( $K$ ) are included in Table 2. Volume fraction versus  $K$  plots are shown in Fig. 2. The  $V^E$  values are fitted to an empirical equation of the form