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

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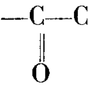
ABSTRACT

Al and Al-Mn alloy were anodized in 1.0 M solution of sulphuric, oxalic, citric and tartaric acids with a variety of current densities (0.50-2.50 a.dm^{-2}) It is found that, the inhibition property of the formed 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^{-2} and time intervals 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.

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_2SO_4 at 20°C for one hour at 250 a.m^{-2}. 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 $CuAl_2$ oxidizes or dissolves faster than aluminium but Koch[3] considered that $CuAl_2$ can be anodized.

The specific resistance of the initial anodic films formed on pure aluminium at 50 - 6000 a.m^{-2} was studied[4] in a range of aliphatic and aromatic acids up to 1.0 M at 25°C. The acids were with and without $—OH, —NH_2, —CH_3,$  $—C(=O)—Cl$ 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 ad 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 (1.0 x 10.0 cm.) were degreased[6] in solution of Na_2CO_3 and Na_3PO_4 at 85°C for 5.0 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 the specimens was carried out in a cell with 10 x 20 cm. in dimensions containing 250 ml of anodizing solution.

The effect of the applied current densities 0.50, 1.00, 1.50 and 2.50 $a.dm^{-2}$ in presence of 1.0 M of anodizing acids sulphuric, oxalic, citric and tartaric at 30°C 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 $a.dm^{-2}$ was also investigated. The anodized specimens were dipped in 30 ml of 3.0 N HCl at 30°C placed in Mylius apparatus[7]. The rise of temperature by time was followed using a 100°C 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°C.

RESULTS AND DISCUSSION

The effect of the anodization current density on the corrosion resistance of Al and Al-Mn alloy was studied in solutions of constant concentration (1.0 M) of the anodizing acid. The time of anodization was 60 minutes in sulphuric and oxalic acids and 5 minutes in citric and tartaric acids. The values of current density applied varied from 0.5 to 2.5 a.dm^{-2}. The variation of the reaction number R.N. (R.N. = $\Delta T_m / t$) along with the corrosion resistance A(A = R.N. - R.N$'$. /R.N.), where t is the time in minutes needed for the temperature to attain ΔT_m, the maximum elevation in temperature, R.N. and R.N$'$. are the reaction numbers of nonanodized and anodized specimens respectively are given in Table 1. It is obvious from that Table, the increase in the anodization current density led to a decrease in the reaction number. This indicates the increase in corrosion resistance of the formed anodic film with the current density of anodiaztion. The conclusion is that by increasing the anodization current density, film properties were improved and its corrosion resistance increased. The relative decrease (A) in reaction number (R.N.) with the vaiiation of anodization current density shown in Table 1 is considered as a measure of the corrosion resistance of the anodic film. Generally, the inhibition property of formed anodic films on both Al and Al-Mn increased by increasing the current density of anodization in the studied acids.

Table 1: (R.N.) and A (in brackets) values for Al and Al–Mn anodized for one hour in 1.0 M H_2SO_4 and oxalic acids and for 5.0 minutes in citric and tartaric acids at different current densities.

Current density a.dm^{-2}.	H_2SO_4		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)

The effect of anodization current density on A is greater in case of anodization in citric and tartaric acids (Al and Al-Mn). Anodization of Al and Al-Mn in oxalic and sulphuric acids at differenet current densities led to the formation of anodic films with smaller changes in their corrosion resistance. These observations may be explained by the variation in the film thickness. In case of anodization in oxalic and sulphuric acids, the anodic film is of the porous type, since the voltage drop across the anodization cell does not vary very much with time. Thus, the increase in current density of anodization may lead to formation a greater number of porous on unit surface area together with greater thickness of the film[8]. The observed effect of current density in citric and tartaric acids on the film properties can be explained on the basis of the film packing, its cohesion and compactness.

The relation log ΔT - 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 a representative results. The constants a and b of equation[9] $t = a + b \log \Delta T$ were evaluated and the relative decrease in the corrosion rate (A) of the anodic film was calculated and given in Tables 2 and 3 using the equations[9] $A = (1 - a/a') \times 100$ and $A = (1 - b/b') \times 100$ where a,b,a′ and b′ are constants in equation $t = a + b \log \Delta T$ for the nonanodized and anodized specimens respectively. In Tables 2 and 3, A_1 is characteristic for the first moment of corrosion. A_2 is the relative decrease in the corrosion rate of the film during its dissolution. A_3 is the same value for the dissolution of the metal surface after removal of the anodic film. ΔT^* is the elavation in temperature at which the inflection in the straight line relations log ΔT — t takes place indicating the transition of the dissolving phase, most probably from the oxide to the metal. According to the data reported in Tables 2 and 3, the values of A generally increased by increasing the current density of anodization. A_3 was always lower than the other two values of A_1 (at $\Delta T = 0.5\,^{\circ}C$) and A_2 (at $\Delta T < T^*$).

For the anodic films of the porous type formed in sulphuric and oxalic acids A_3 (at $\Delta T > T^*$) is distinctly lower than the corresponding value for the barrier type anodic films formed in citric and tartaric acids. This could be caused by the very resistive barrier type films which does not dissolve so easily as the porous films. The resistance of the barrier type films makes the corrosion of the specimens proceeds under this film starting from any defect of crack on the surface. Thus, at ΔT^*, the metal surface is not completely activated, but may be partially free from the highly resistive barrier anodic film. Therefore, A_3 ($\Delta T > T^*$) for anodized specimens in citric and tartaric acids is higher than the corresponding value for specimens anodized in sulphuric and oxalic acids.

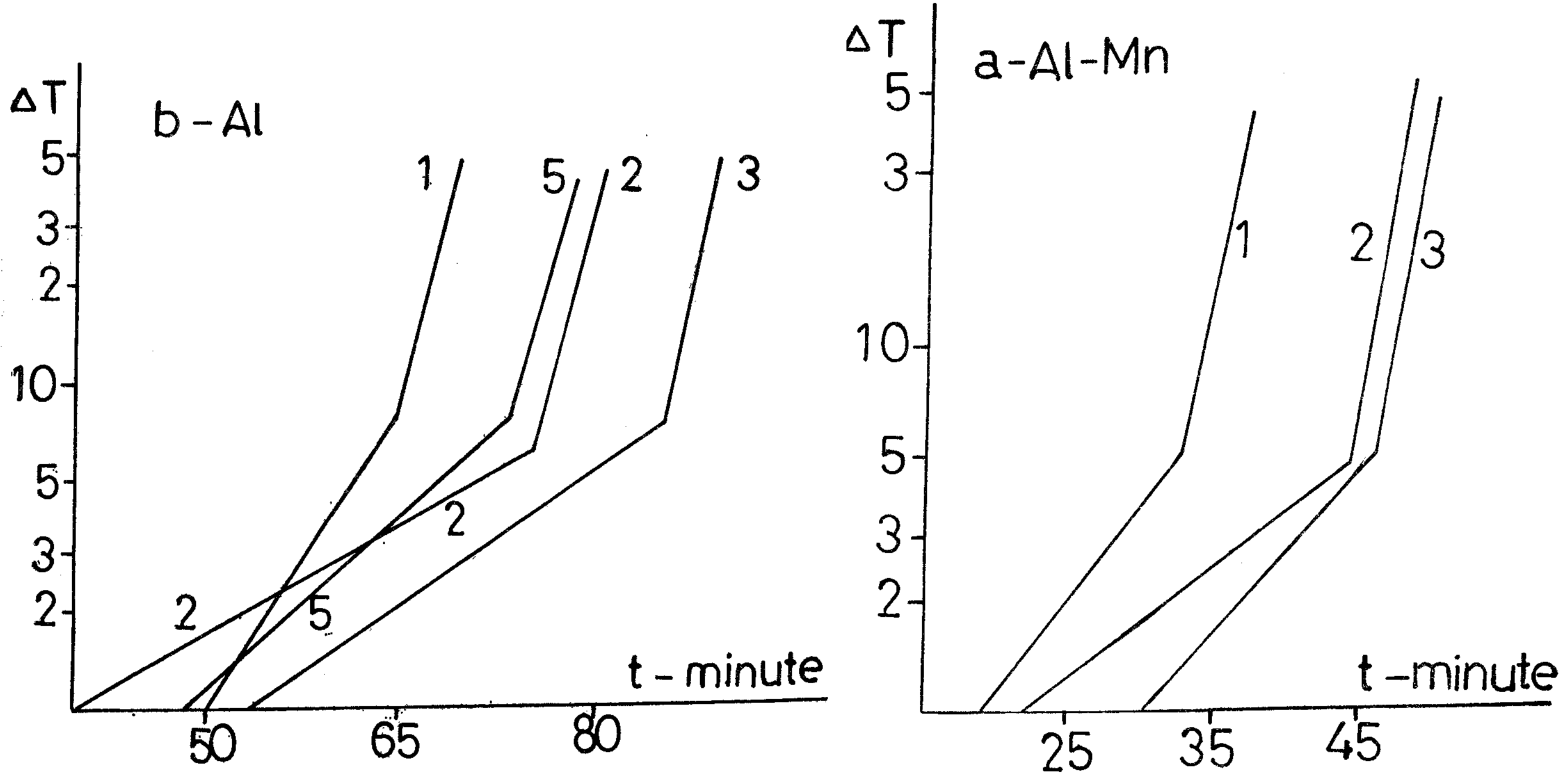


Figure 1: log ΔT–t curves for;

a– Al–Mn: 1,2–1,5 and 3– 2.50 a.dm^{-2}.

b– Al: 1– 0.25, 2–0.50, 3– 0.75, 4– 1.0 and 5– 1.50 a. dm^{-2} anodized in 1.0 M sulphuric acid at 30°C.

Table 2: a,b constants and relative decrease in corrosion rate A of Al and Al-Mn anodized in 1.0 M H_2SO_4 at different current densitises.

	C.d. $a.d.m^{-2}$	a_1	b_1	ΔT*	b_2	$A_1\%$	$A_2\%$	$A_3\%$
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	30.25	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. $a.dm.^{-2}$	a_1	b_1	ΔT*	b_2	$A_1\%$	$A_2\%$	$A_3\%$
A	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
A -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

The effect of anodiztion time on the corrosion resistance of Al and Al-Mn was also studied in 1.0 M acid solution at 30°C and 1.0 $a.dm^{-2}$ for 10–60 minutes. The results of ΔT-t measurements indicated that the increase in anodization time led to a decrease in reaction number and accordingly to an increase in the corrosion resistance of the anodic films. The relative decrease in reaction number (A) calculated as mentioned before for Al and Al-Mn anodized in sulphuric and oxalic acids are given in Table 4 as a representative data. The results of $t_{1/2}$ (the time intervals at which $T = \Delta T_m/2$) are reported in Table 5 where it is evident that by increasing the time of anodization, $t_{1/2}$ increased. This is quite clear for anodized Al and Al-Mn in sulphuric and oxalic acids. In case of citric and tartaric acids, an irregular values of $_{1/2}$ were obtained which did not give a definite relationship between $t_{1/2}$ and anodization time. These facts may be explained on the basis of film thickness which increased as time of anodization increased, especially in case of sulphuric and oxalic acids where the film formed is of porous type.

Table 4: R.N. and A (in brackets) values for Al and Al–Mn anodized for time intervals in 1.0 M H_2SO_4 and oxalic acids.

Time of anodization, minutes	H_2SO_4		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 $a.dm^{-2}$ for time intervals.

Time of anodizati- minutes	H_2SO_4		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 straight lines of the relation $t = a + b \log \Delta t$ for different time periods of anodization of Al and Al-Mn in the four studied acids are obtained and the relative decrease in the corrosion rate (A) was calculated (where the anodization is carried out in H_2SO_4) as mentioned before. In Table 6, A_2,A_2,A_3 and ΔT^* have the same defination given in this work. The values of A_1 and A_2 were always close to each other but much higher than A_3. This is in accord within the idea that at $\Delta T > T^*$, the active metal surface is the phase interacting with the aggressive medium (3.0 N HCl), below ΔT^*, the anodic film is still existing and thus A is of considerable value.

The dissolution of Al and Al-Mn anodized in citric and tartaric acids for different time intervals gave A_3 of a considerable value. This may be attributed to the basically different type of the anodic film formed in these acids. It seems that dissolution of the anodized specimens in these acids takes place via a subsurface mechanism, while the anodic film extremely stable in the aggressive medium. Thus, the inflection at ΔT^* may be due to the partial and not complete elimination of the anodic film. That is why the values of ΔT^* do not vary in a regular manner as given in Table 6.

Table 6: a,b constants and relative decrease in corrosion rate A of Al and Al–Mn anodized in 1.0 M H_2SO_4 for time intervals.

	Time minutes	a	b_1	ΔT^*	b_2	$A_1\%$	$A_2\%$	$A_3\%$
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

REFERENCES

1. G.C. WOOD and A.J. BORCK, Trans. Inst. Metal Finishing, 44, 189, 1966.

2. F. KELLER and J.D. EDWARDS, Iron Age, 156, 75, 1945.

3. N. FISCHER, N. BUDILOFF and L. KOCH, Korrosion und Metallschutz, 16, 236, 1940.

4. T. MURAMAKI, N. BABA and S. TAJIMA, Aluminium Federation, London, p. 37, 1967.

5. J.M. KAPE, Electroplating and Metal Finishing, 14, 407, 1961.

6. AZ. KIZ and A.M.S. EL-DIN, Corr. Sci., 55, 489, 1965.

7. F. MYLIUS, Z. Metalk, 14, 233, 1922.

8. J.P. O'SULLIVAN and G.C. WOOD, Proc. Roy. Soc., A 317, 511, 1970.

9. G.A. NOUBI, A. AWAD and F.M. EL-CHEIKH, Indian J. Technol., 127, 1980,

G.A. NOUBI, F.M. EL-CHEIKH AND H. MANSOUR, J. Electrochem. Soc. India, 32, 181, 1983.