

# THE DETERMINATION OF THE VARIABLES OF HIGH RESPONSE ON THE ANODIZING OF ALUMINUM-MAGNESIUM ALLOY 5052 (STATISTICAL ANALYSIS)

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## ABSTRACT

*Aluminum-magnesium alloy of type 5052 had been anodized using sulfuric acid as an electrolyte. Four variables, which were considered as the most important variables, were studied. These variables are current density between 2-3 amp/dm<sup>2</sup>; electrolyte concentration between 2-6 N; electrolyte temperature between 15-25 °C; and time of exposure between 20-60 minutes. In previous study the author (Kaseer et al, 2001) correlates the four studied variables with the thickness of the anodized film by a second order polynomial. It was found that the current density and time of exposure have positive significance of great importance on the anodized film while the concentration and temperature of electrolyte have negative significance of minor effect. Herein, a statistical analysis for the results of the anodizing of aluminum-magnesium alloy 5052 was attained to find the most significant effects on the objective function (i.e. the film thickness of the anodized aluminum). The results of the statistical analysis had also postulate that time of exposure (i.e.  $X_1$ ) has the most significant effect on the thickness of the anodic film, and in lesser degree the current density ( $X_2$ ) and electrolyte concentration ( $X_3$ ) while the electrolyte temperature ( $X_4$ ) has no significant effect.*

## INTRODUCTION

When the anode is Aluminum, the cathode in commercial practice, is either aluminum or lead. The current is passed through the electrolyte, such as H<sub>2</sub>SO<sub>4</sub>, most of the oxygen that would have been liberated combines with the aluminum to form a layer of porous aluminum oxide while hydrogen is liberated at the cathode. The amount of aluminum oxide formed is directly proportional to the current density and time, i.e. to the quantity of electric current used. The progress of the anodic coating depends on the chemical composition of the anodizing electrolyte and the chosen conditions of electrolysis (Henely, 1982).

The anodizing process using sulfuric acid was first used in Russia and U. K. (Wermilk and Pinner, 1972). Due to low cost of H<sub>2</sub>SO<sub>4</sub> and simplicity of controlling the operating conditions, Sulfuric acid was widely used as an electrolyte for anodizing among other processes (Franklin, 1961). Grower and Brien patented this process in 1927 that provides anodic film suitable for a wide range of products since the characteristics of the film can be changed predictably by varying the acid concentration, temperature and current density. Because of low cost, ease of control and excellent film characteristics, the process can be

used on every kind of product made of aluminum (Franklin, 1961). At low temperatures (-5 to 5 °C), the sulfuric acid process gives very hard coating known as "hard anodizing" and is widely employed in the engineering industry (Henely, 1982).

In this paper a statistical analysis was done to find the significance of the affecting variable on the formation of anodic oxide film of aluminum-magnesium alloy (5052) that was previously treated by the author using sulfuric acid anodizing process.

## EXPERIMENTAL WORK

### Materials

The chemical composition of the alloy was analyzed by Central Organization for Standardization and Quality Control and its composition was found as follows: 0.006% Cu, 0.222% Fe, 0.037% Mn, 0.010% Zn, 2.374% Mg, 0.1% Si, and 97.251% Al.

The specimen was prepared in a sheet form of 30 mm thickness with an overall surface area of 47.2 cm<sup>2</sup> (0.472 dm<sup>2</sup>). For alkaline etching step and for acidic etching, 5 % NaOH solution, and 15 % HNO<sub>3</sub> solution was used respectively.

## Anodizing Cell

For the anodizing cell, a rectangular box made of polyethylene to resist the action of sulfuric acid was used. Aluminum weir jigs designed to hold the two electrodes (anode and the cathode) were fixed in the cell by racks. Direct current power supply (type, mi-dual power supply, TF 2158) was incorporated with the anodizing cell to supply current to the electrodes of maximum of 2 Amp and voltage of 30 volt. To maintain good mixing of the electrolyte solution and to prevent temperature layering in the anodizing cell, a mechanical stirrer (type, Heidolph 50110) was installed. Cooling system consists of a rectangular cooling bath and Grant instrument (type SU6) for pumping water incorporated with an immersed glass coil that installed inside the anodizing cell was installed. Figure (1) shows a schematic diagram for the anodizing assembly. To heat up the chemicals at the desired temperature through etching and sealing steps a mantel heater was used.

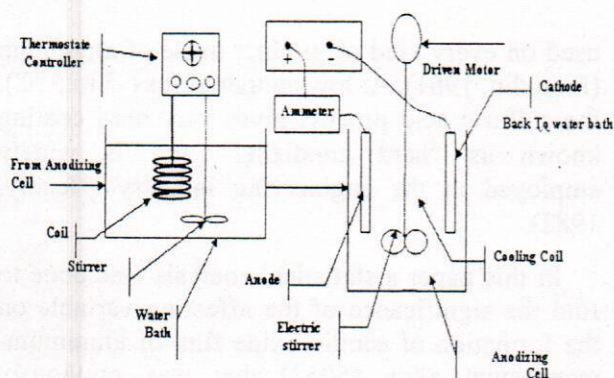


Fig. (1) Schematic diagram for the whole assembly of the anodizing apparatus

## Experimental Procedure

Raw material of aluminum-magnesium alloy was prepared in sheet form of dimensions (100x20x3) mm. The edge of the prepared specimens was chamfered by a grinding wheel. Etching by a 5 % NaOH solution (density = 1.06 gm/cm<sup>3</sup>) for 5 minutes at temperature 40-50 °C was commenced. Then, rinsing the specimen with tap water followed with distill water was carried out. To remove the black layer that was formed and also to activate the surface, the specimen was immersed in 15 % HNO<sub>3</sub> solution (density = 1.085 gm/cm<sup>3</sup>) for 10 seconds at room

temperature. Once again, the specimen was rinsed with distill water. After each rinsing the specimen was subjected to a stream of hot air for drying. Before ensuing anodizing step the anode and the cathode are well connected to the power supply by aluminum weir jigs. The mechanical stirrer, water bath temperature, concentration of electrolyte and current density were adjusted at pre-designed conditions. After anodizing step (sulfuric acid process), the specimen was rinsed with tap water to remove the residual of electrolyte solution. Sealing the initial porous was performed by immersing the specimen in a flask filled with hot water at 95 °C for 20 minutes. Before sealing the initial porous, colouring of the specimens was commenced by potassium dicromate (45 g/l). The colouring step was carried out at 60 °C and lasted for 15 minute. Afterward, drying of the specimen was performed by hot air then thickness of the anodized specimen was measured. Thickness-testing meter of type Posi Pilot ® was used for measuring film thickness.

## Statistical Analysis

In this part of the paper, the principles governing the construction and analysis of an orthogonal central composite design in which the response (*y*) is the film thickness of the anodized film and the variables (*X<sub>k</sub>*) are the current density, electrolyte concentration, temperature of electrolyte and time of contact, hereafter called *X<sub>1</sub>*, *X<sub>2</sub>*, *X<sub>3</sub>* and *X<sub>4</sub>* respectively. Table (1) shows the orthogonal central composite design presented according to the standard order; variable values have no dimension. The level values of natural variables are summarized in Table (2). The coded and natural variables are related by following relation (Box *et al*, 1978):

$$X_{\text{coded}} = \frac{[X_{\text{actual}} - X_{\text{center}}]}{\left[ \frac{X_{\text{center}} - X_{\text{min}}}{\sqrt{k}} \right]}$$

The experimental data as represented in Table 1 are introduced to a nonlinear regression estimation adapting Statistica Software in order to estimate the coefficient of the 2<sup>nd</sup> order polynomial that proposed to relate the objective variable with the studied ones that was previous work as follows (Kaseer *et al*, 2001):

$$Y = 16.10006 + 4.224980X_1 - 1.94168X_2 - 0.091682X_3 + 7.366642X_4 + 0.695807X_1^2 + 0.045808X_2^2 - 0.054200X_3^2 - 0.004191X_4^2 + 0.249996X_1X_2 - 2.75001X_1X_3 + 1.662498X_1X_4 + 1.57500X_2X_3 - 2.4625X_2X_4 + 0.037495X_3X_4 \quad (1)$$

Table (1) Values of the experimental measured and estimated thickness of the oxide film

Exp. No.	Coded Variable				Real Variable				Exp. Thickness	Predicted Thickness	Error $e_i^*$ (Y - $\hat{Y}$ )
	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	Current Density (Amp/0.5dm <sup>2</sup> )	Conc. (equiv./l.)	Temp. (°C)	Time (min)	Y (Micro)	$\hat{Y}$ (Micro)	
1	-1	-1	-1	-1	1.125	3	17.5	30	3	5.5	-2.5
2	+1	-1	-1	-1	1.375	3	17.5	30	18.1	15.6	2.5
3	-1	+1	-1	-1	1.125	5	17.5	30	1.5	2.9	-1.4
4	+1	+1	-1	-1	1.375	5	17.5	30	14.5	14.0	0.5
5	-1	-1	+1	-1	1.125	3	22.5	30	5.4	7.6	-2.2
6	+1	-1	+1	-1	1.375	3	22.5	30	9.7	6.7	3.0
7	-1	+1	+1	-1	1.125	5	22.5	30	10.3	11.3	-1.0
8	+1	+1	+1	-1	1.375	5	22.5	30	10.2	11.4	-1.2
9	-1	-1	-1	+1	1.125	3	17.5	50	22.6	21.7	0.9
10	+1	-1	-1	+1	1.375	3	17.5	50	37.1	38.5	-1.4
11	-1	+1	-1	+1	1.125	5	17.5	50	3.9	9.3	-5.4
12	+1	+1	-1	+1	1.375	5	17.5	50	38.9	27.1	11.8
13	-1	-1	+1	+1	1.125	3	22.5	50	21.1	24.0	-2.9
14	+1	-1	+1	+1	1.375	3	22.5	50	30.8	29.0	1.8
15	-1	+1	+1	+1	1.125	5	22.5	50	15.0	17.8	-2.8
16	+1	+1	+1	+1	1.375	5	22.5	50	24.7	24.6	0.1
17	-2	0	0	0	1.000	4	20	40	17.8	10.4	7.4
18	+2	0	0	0	1.5	4	20	40	22.9	27.3	-4.4
19	0	-2	0	0	1.25	2	20	40	19.7	20.1	-0.4
20	0	+2	0	0	1.25	6	20	40	15.8	12.3	3.5
21	0	0	-2	0	1.25	4	15	40	17.3	16.0	1.3
22	0	0	+2	0	1.25	4	25	40	17.4	15.6	1.8
23	0	0	0	-2	1.25	4	20	20	1.2	1.3	-0.1
24	0	0	0	+2	1.25	4	20	60	33.9	30.8	3.1
25	0	0	0	0	1.25	4	20	40	16.1	16.1	0.0
26	0	0	0	0	1.25	4	20	40	16.1	16.1	0.0
27	0	0	0	0	1.25	4	20	40	16.1	16.1	0.0
28	0	0	0	0	1.25	4	20	40	16.1	16.1	0.0
29	0	0	0	0	1.25	4	20	40	16.1	16.1	0.0
30	0	0	0	0	1.25	4	20	40	16.1	16.1	0.0
31	0	0	0	0	1.25	4	20	40	16.1	16.1	0.0

Table (2) Working range of coded and corresponding real variables

Coded Level	Current Density (Amp/0.5dm <sup>2</sup> )	Concentration (equiv./l.)	Temperature (°C)	Duration Time (min)
-2	1.00	2	15.0	20
-1	1.125	3	17.5	30
0	1.250	4	20.0	40
1	1.375	5	22.5	50
2	1.500	6	25.0	60

From Eq. (1), it is possible to compute the estimated values,  $\hat{Y}_i$ , and the corresponding residuals  $e_i = (Y_i - \hat{Y}_i)$  as listed in the last column in Table 1. An estimate of the experimental error variance ( $S_r^2$ ) is obtained by dividing the residual sum of squares  $\sum e_i^2$  by  $\gamma$  the number of degree of freedom (number of experiments minus number of coefficients in Eq 1):

$$S_r^2 = \frac{\sum e_i^2}{\gamma} \quad (2)$$

The estimated variances of coefficient  $S_{bv}^2$  given in Table 3 are then calculated by the following formula:

$$S_{bv}^2 = S_r^2 / \sum V_i^2 \quad (3)$$

The significance of effects may be estimated by comparing the values of the ratio ( $b_v^2 / S_{bv}^2$ ) to the critical value [ $F_{0.95}(1,16) = 4.48$ ] of the F distribution at 95 % level of confidence with 1 and 16 degree of freedom.

Table (3) Analysis of variance of variable effects

	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>4</sub>	X <sub>1</sub> X <sub>2</sub>	X <sub>1</sub> X <sub>3</sub>	X <sub>1</sub> X <sub>4</sub>	X <sub>2</sub> X <sub>3</sub>	X <sub>2</sub> X <sub>4</sub>	X <sub>3</sub> X <sub>4</sub>	$\eta_1^2$	$\eta_2^2$	$\eta_3^2$	$\eta_4^2$
B	4.22	-1.94	-0.09	7.37	0.23	-2.75	1.66	1.57	-2.46	0.07	0.65	0.64	-0.54	-0.04
S <sup>2</sup>	466	466	466	466	729	729	729	729	729	729	0.02	0.03	0.04	0.02
F-value B/S <sup>2</sup>	36.73	7.76	0.17	111.67	0.86	10.37	3.79	3.40	8.32	0.02	0.64	0.03	0.04	0.02
F(1,16) 0.95 Confidence	S	S	NS	S	NS	S	NS	NS	S	NS	NS	NS	NS	NS

Accordingly Table 3 show that only the effects of X<sub>1</sub>, X<sub>2</sub>, and X<sub>4</sub> and the interaction effects of X<sub>1</sub>X<sub>3</sub>, X<sub>2</sub>X<sub>4</sub> are significant. The best fitting response function is then reduced to more conveniently form as follow:

$$Y = 16 + 422X_1 - 194X_2 + 736X_4 - 275X_1X_3 - 246X_2X_4 \quad (4)$$

## RESULTS AND DISCUSSION

The effects of each variable on the film thickness of the anodized specimens are shown in Figs (2) to (5). In Fig (2), It is clearly seen that the current density has a significant effect on the thickness of the oxide film, which is extremely incorporated with increasing the current density. While, increasing the electrolyte concentration has a negative significance on the film thickness as distinguished from Fig (3). This negative dependence can be attributed to the nature of electrolyte since sulfuric acid is a dehydrator agent in its nature, therefore increasing its concentration will capture more water molecules that lead to decrease the free oxygen to form the oxide film.

In studying Fig (4), it is clearly shown that the temperature of the electrolyte has low negative dependence on the film thickness. No such dependence was found from statistical analysis, Table (3). This observation was came in contrary to that submitted by Henely (1982) who states the

influence of anodizing temperature on the anodic film formation. This discrepancy was contributed to the range of temperatures that was adopted since the dissolution rate is equated the growth rate of the anodic film no significant dependence of temperature on oxide film thickness was found. It was ascertained that the time of exposure was the most significant variable on the film thickness. Also Fig (5) show that increasing the time of exposure increases the film thickness since the amount of the oxide film is proportionally related to the quantity of the electric current that becoming bigger with longer time of exposure. As previously shown Eq (4) sponsored these main effects of  $X_1$ ,  $X_2$ , and  $X_3$  on the anodic film formation.

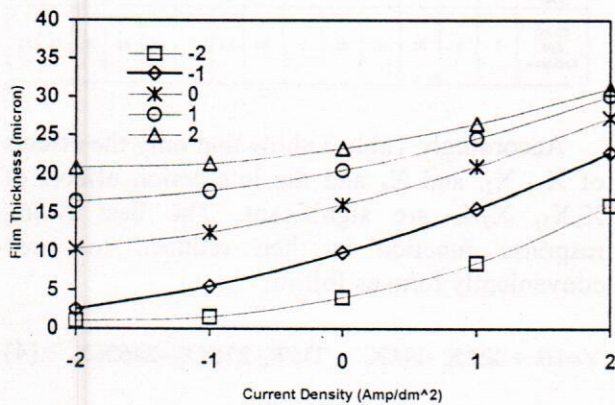


Fig. (2) The effect of current density on film thickness at different concentrations, temperatures and times of exposure

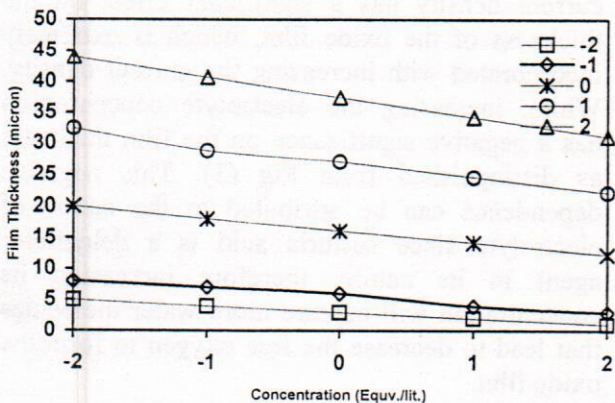


Fig. (3) The effect of concentration on film thickness at different current densities, temperatures and times of exposure

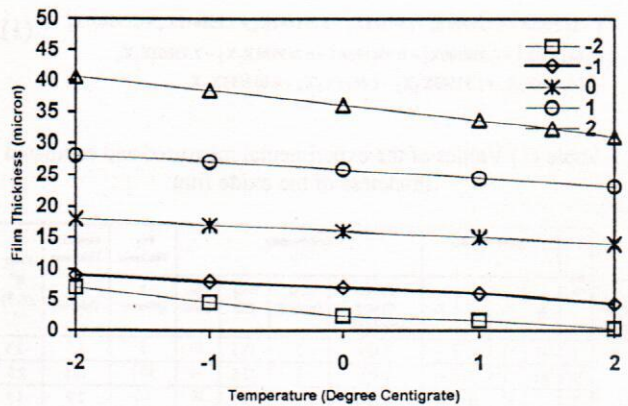


Fig. (4) The effect of temperature on film thickness at different current densities, concentrations and times of exposure

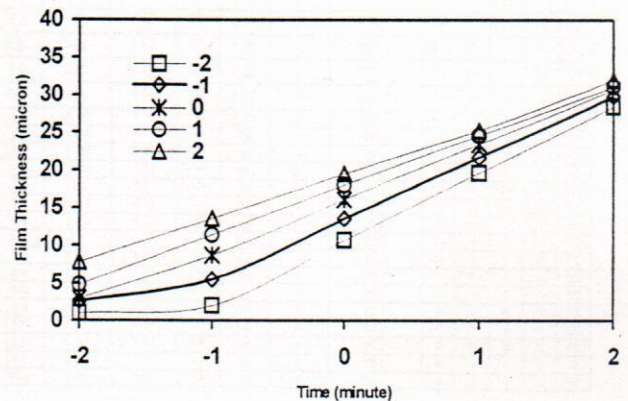


Fig. (5) The effect of time of exposure on film thickness at different current densities, concentrations and temperatures

A comparison study was outlined from Figs (6) to (11) to study the interference interaction between the studied variables. According to Eq (4) only  $X_1X_3$  and  $X_2X_4$  had shown significant interaction dependencies. This was ascertained as shown in Fig (6), since  $X_1$  and  $X_3$  have shown significant dependence on each other (i.e., the curves shows different slopes). Also in Fig (7) the interaction significance between  $X_2$  and  $X_4$  was found. Eventually, as outlined before from statistical analysis study, Figs (8) to (11) ensue no such interaction.

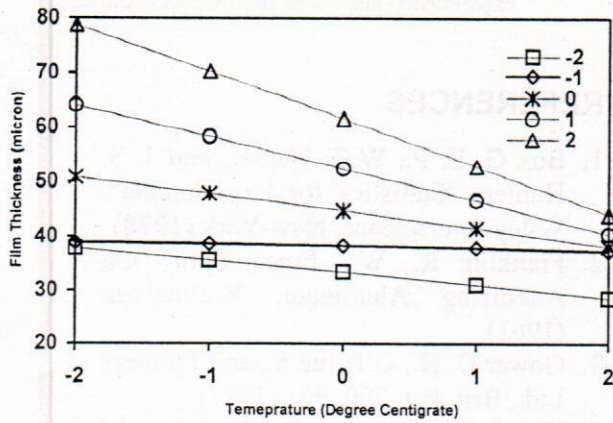


Fig (6) The effect of temperature and current density on film thickness, concentration and time of exposure being constant

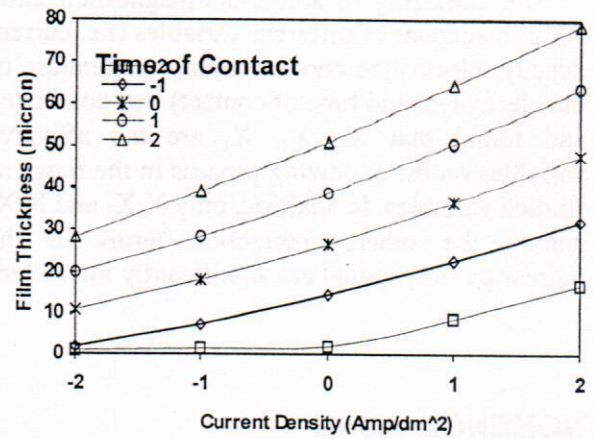


Fig (9) The effect of current density and time of exposure on film thickness, concentration and temperature being constant

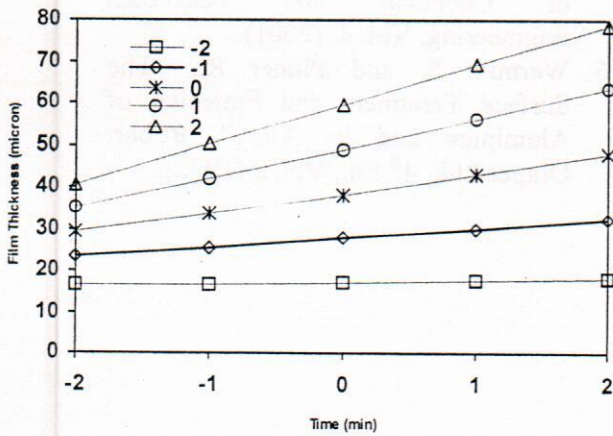


Fig (7) The effect of time of exposure and concn. on film thickness, current density and temperature being constant

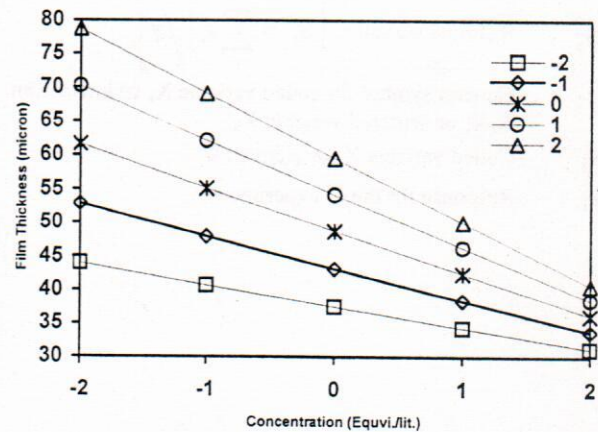


Fig (10) The effect of concentration and temperature on film thickness, current density and time of exposure being constant

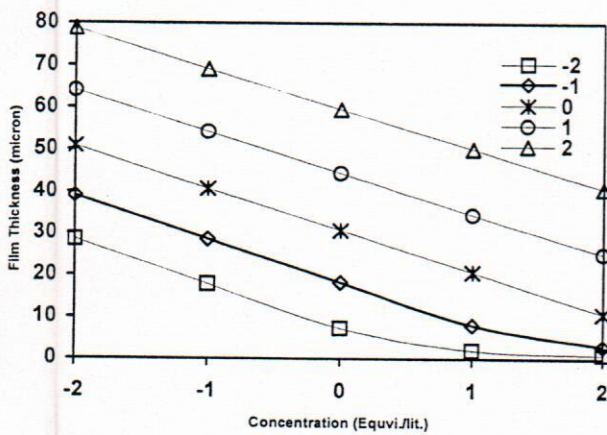


Fig (8) The effect of concentration and current density on film thickness, temperature and time of exposure being constant

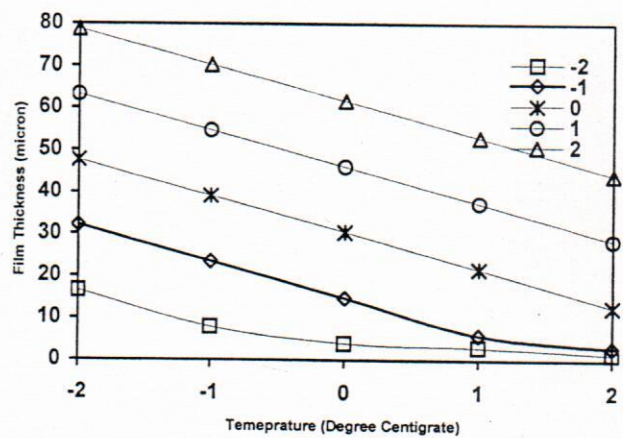


Fig (11) The effect of temperature and time of exposure on film thickness, current density and temperature being constant

## CONCLUSIONS

The anodizing of aluminum-magnesium alloy 5052 in account of different variables (i.e. current density, electrolyte concentration, temperature of the electrolyte and time of contact) was conducted and found that  $X_1$ ,  $X_2$ ,  $X_4$  are the affective variables on the anodizing process in the range of studied variables. In addition, only  $X_1X_3$  and  $X_2X_4$  among the others interaction terms in the regression polynomial are significantly interacted.

## NOMENCLATURE

$b_v$	Coefficient of the estimated model
$e_i$	Residual of the $i^{\text{th}}$ experiment: $e_i = Y_i - \hat{Y}_i$
N	Normality
$S_{b_v}^2$	Estimated variance of coefficient $b_v$
$S_r^2$	Residual variance: $S_r^2 = \sum_i e_i^2 / \gamma$
V	General symbol for coded variable $X_k$ or interaction $X_kX_k$ or centered variable $X_k^2$
$X_k$	Coded variable X for element k
$Y_i$	Response for the $i^{\text{th}}$ experiment

$\hat{Y}_i$	Estimated response for the $i^{\text{th}}$ experiment
$\gamma$	Number of degrees of freedom = number of experiments- number of coefficients in the eq (1)

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