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INFLUENCE OF PROCESS PARAMETERS ON POROSITY AND PORE DENSITY DURING SULFURIC ACID ANODIZATION OF AA 6061

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ABSTRACT

This study focuses on optimizing anodization parameters based on the Taguchi method to minimize porosity and pore density. Experiments have been conducted using the L16 orthogonal array in an anodization tank. AA 6061 specimens were used to conduct the experiments and each experiment is repeated three times and to ensure accuracy of the output. The statistical methods of signal to noise ratio (SNR) and the analysis of variance (ANOVA) are applied to investigate effects of electrolyte concentration, electrolyte temperature and voltage on porosity and pore density. Results of this study indicate that the voltage has the most significant effect on porosity and electrolyte temperature is the significant factor affecting pore density. Confirmation tests were also carried out to check the validity of the results.

KEYWORDS: AA 6061, Anodization, Porosity, Taguchi Optimization Methods, ANOVA

INTRODUCTION

The anodizing process of metals has been used by industries to protect metal components from corrosion. During this electro-chemical process the surface chemistry of the metal is changed, via oxidation, to produce an anodic oxide layer that is thick enough to stifle further oxidation. Two types of anodic Al oxide exist; the first is a non-porous barrier layer that is thin, hard, and wear resistant and behaves as an electrical insulator. The second, a thicker porous oxide structure, is called the anodic aluminum oxide (AAO) layer. This layer structure has a high aspect ratio and consists of a porous structure. In engineering applications, this pore structure must be sealed to prevent corrosion. Anodizing is widely affected by change in voltage, bath concentration and temperature. An optimized parameter combination can result in less porous structure.

Belwalkar et al. (2008) conducted a study on anodization of aluminium alloy in sulfuric acid. It was found that the pore size increased in direct proportion with the applied voltage and inversely with the electrolyte concentration while the interpore distance increased linearly with the applied voltage. Ono and Masuko (2003) anlaysed the effects of various electrolytes such as sulfuric acid, phosphoric acid, oxalic acid and chromic acid on the formation of nanopores in the aluminium and concluded that the pore diameters formed at an identical voltage in different electrolytes are larger in the order: sulfuric acid<oxalic acid<chromic acid<phosphoric acid.

Sulka and Parkola (2007) performed a study on aluminium alloy anodization in sulfuric acid. It was found that the pore diameter increases with increasing temperature and the interpore distance decreases (or pore density increases) with increasing temperature of anodization for a voltage of 25V. Aerts et al. (2007) analyzed the effect of temperature on the microhardness during sulfuric acid anodization of aluminium and concluded that the microhardness of the anodic films progressively decreased with increasing electrolyte temperature. Also with increasing electrolyte temperature the structure became more open with increasing pore diameters and there is interlinking between the pores at higher temperature.

Sulka and Parkola (2006) conducted a study on aluminium alloy anodization in sulfuric acid. The pore diameter and the interpore distance increase linearly with increasing cell potential. The porosity of the anodic alumina structure depends on the applied anodizing potential. Bai et al. (2008) investigated the influences of anodizing variables, such as applied voltage, solution temperature, oxalic acid concentration, agitation rate, and sulfuric acid concentration, on the average pore diameter using Fractional Factorial Design (FFD). The applied voltage, and sulfuric acid concentration were found to be the key factors affecting the pore diameter of AAO films.

Thus electrolyte concentration, electrolyte temperature and voltage are the key factors determining the size of the pores and interpore distance which in turn determines the porosity and pore density. The effect of these factors on sulphuric acid anodization of AA 6061 has not been investigated till date.

MATERIALS AND METHODS

Work Piece

For determining porosity, pore density and for FE-SEM analysis disk shaped samples of AA 6061 having diameter 46 mm and thickness 10 mm were used. A through hole of diameter 4 mm is made on the work piece at a distance of 20mm from the centre in order to facilitate jigging. The composition and mechanical properties of AA 6061 is shown in Table 1 and Table 2 respectively.

Table 1: Chemical Composition of AA 6061

Al	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
95.85-98.56	0.4-0.8	0.7	0.15-0.4	0.15	0.8-1.2	0.04-0.35	0.25	0.15 Max

Table 2: Mechanical Properties of AA 6061

Density (g/cc)	2.7
Melting Point Range (deg C)	582-652
Ultimate Tensile Strength (MPa)	310
Yield Strength (MPa)	276
Hardness (HRC)	40
Thermal Conductivity (W/m.K)	167

Experimental Details

Prior to anodizing, the samples were vapour degreased in Trichloro Ethylene solution at 85^{o}c for 20 minutes, followed by alkaline etching in 5% NaOH solution (by weight) at 55^{o}c for 30 seconds. The samples were then made to undergo a desmutting treatment in a solution containing standard HNO_3 (70% concentration) at room temperature for 60 seconds. After all the pretreatments, the samples were chemical polished in 95% phosphoric acid and 5% nitric acid at 70^{o}c under an agitation rate of 750 rpm for 30 seconds.

The polished specimens were then jigged using clean aluminium wire into the anodization tank. Anodizing time was fixed as 45 minutes for all the experiments. The process parameters like electrolyte temperature and voltage were varied by the control panel and electrolyte concentration is varied as needed according to the experiment. After anodizing, the samples were rinsed and cleaned in pure running water for 30 seconds, and then dried at room temperature. The pore diameter and interpore distance of the porous anodic aluminium oxide were measured by a Field- Emission Scanning Electron Microscope (FE-SEM, Hitachi SU6600).

Measurement of Porosity and Pore Density

Porosity ($\propto$) is defined as the ratio of the surface area occupied by pores to the whole surface area of the sample. For the close-packed hexagonally arranged lattice of pores, porosity can be calculated from

$$\propto = \frac{\pi}{2\sqrt{3}}\left(\frac{D_p}{D_i}\right)^2 \tag{1}$$

Where, D_p is the pore diameter and, D_i is the interpore distance

Pore density (n) is defined as a total number of pores on 1µm^2 of surface area. Pore density,

$$n=\frac{10^6}{\sqrt{3}\times D_i^2} \tag{2}$$

Where, D_i is the interpore distance. The pore diameter and interpore distance are taken from FE-SEM images.

Taguchi Experiment: Design and Analysis

DOE is a systematic approach to investigation of a system or process. A series of structured tests are designed in which planned changes are made to the input variables of a process or system. The effects of these changes on a pre-defined output are then assessed. For each input variable, a number of levels are defined that represent the range for which the effect of that variable is desired to be known. An experimental plan is produced which tells the experimenter where to set each test parameter for each run of the test. The response is then measured for each run.

The experimental design proposed by Taguchi involves using orthogonal arrays to organize the parameters affecting the process and the levels at which they should be varies. Instead of having to test all possible combinations like the factorial design, the Taguchi method tests pairs of combinations. This allows for the collection of the necessary data to determine which factors most affect product quality with a minimum amount of experimentation, thus saving time and resources.

Experimental Procedure

For studying the degree of influence of the process parameters during anodization of AA 6061 in sulphuric acid, three factors, each at four levels are taken as shown in Table 3. In this research, sixteen experiments were conducted at different parameter levels. For this L16 orthogonal array was used, which has sixteen rows corresponding to the number of tests (Table 4). The pore diameter and interpore distance taken from the FE-SEM image (Figure 1) are shown in Table 5 along with the corresponding porosity and pore density.

Table 3: Anodization Process Parameters

		Levels and Values				Responses
Parameter	**Unit**	**1**	**2**	**3**	**4**	
Electrolyte Concentration	% wt/vol	14	16	18	20	1. Porosity 2. Pore density
Electrolyte temperature	˚C	5	10	15	20	
Voltage	V	14.5	18	21.5	25	

Table 4: Taguchi L16 Orthogonal Array

Experiment	Electrolyte Concentration (%wt/vol)	Electrolyte Temperature (˚c)	Volt (V)
1	1	1	1
2	1	2	2
3	1	3	3
4	1	4	4
5	2	1	2
6	2	2	1
7	2	3	4
8	2	4	3
9	3	1	3
10	3	2	4
11	3	3	1
12	3	4	2
13	4	1	4
14	4	2	3
15	4	3	2
16	4	4	1

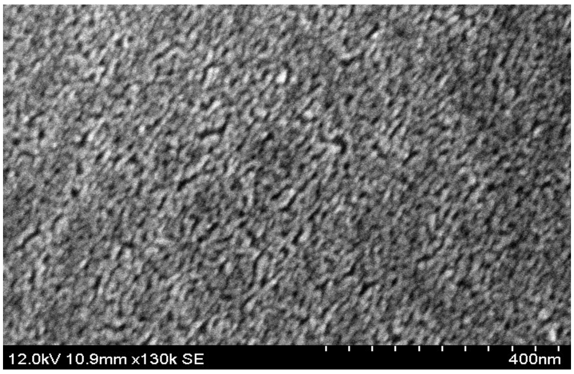


Figure 1: FE-SEM Image of the Porous Anodic Oxide Formed at Electrolyte Concentration of 14 wt % / Volume, Electrolyte Temperature of 5ºC and Voltage of 14.5 V

Table 5: Taguchi L16 Orthogonal Array for Porosity and Pore Density

Electrolyte Concentration (%wt/ vol)	Electrolyte Temperature (˚C)	Volt (V)	Pore Diameter, D_p (nm)	Interpore Distance, D_i (nm)	Porosity (%)	Pore Density (μm^2)
14	5	14.5	7.36	19.06	13.52	1590
14	10	18	9.10	43.10	4.04	310
14	15	21.5	18.62	53.56	10.96	201
14	20	25	15.04	41.34	12	338
16	5	18	11.14	26.76	15.71	806
16	10	14.5	9.73	23.08	16.11	1083
16	15	25	17.3	26.48	38.71	823

Table 5: Contd.,

16	20	21.5	18.46	36.60	23.07	431
18	5	21.5	7.71	19.92	13.58	1455
18	10	25	9.03	16.60	26.83	2095
18	15	14.5	6.45	21.26	8.34	1277
18	20	18	16.10	62.6	6.01	147
20	5	25	8.02	14.64	27.21	2694
20	10	21.5	20.60	48.94	16.06	241
20	15	18	8.56	21.28	14.67	1275
20	20	14.5	14.28	34.34	15.68	490

RESULTS AND DISCUSSIONS

Analysis of S/N Ratio

The most essential criterion in the Taguchi method for analyzing experimental data is signal/noise ratio. Porosity and pore density was considered as the quality characteristic "smaller is the better".

The S/N ratio values are calculated using equation (3). The porosity and pore density values and their corresponding S/N ratio values are listed in Table 6.

Table 6: Porosity and Pore Density Values along with Their Corresponding S/N Ratio Values

Exp No.	Porosity		Pore Density	
	Porosity (%)	S/N Ratio (dB)	Pore Density (μm^2)	S/N Ratio (dB)
1	13.52	-22.61953	1590	-64.02794
2	4.04	-12.12763	310	-49.82723
3	10.96	-20.79621	201	-46.06392
4	12	-21.58362	338	-50.57833
5	15.71	-23.92352	806	-58.12670
6	16.11	-24.14191	1083	-60.69257
7	38.71	-31.75646	823	-58.30880
8	23.07	-27.26095	431	-52.68955
9	13.58	-22.65880	1455	-63.25726
10	26.83	-28.57241	2095	-66.42368
11	8.34	-18.42332	1277	-62.12382
12	6.01	-15.57750	147	-43.34635
13	27.21	-28.69457	2694	-68.60795
14	16.06	-24.11491	241	-47.64034
15	14.67	-23.32860	1275	-62.11020
16	15.68	-23.90692	490	-53.80392

The S/N ratio for smaller the better is:

$$\frac{S}{N} = -10\log_{10}\left[\frac{1}{n}\sum y^2\right] \qquad (3)$$

Where n is the number of observations and y is the measured output value. The S/N ratio values for porosity by factor level are shown in Table 7 and S/N ratio values for pore density by factor level are shown in Table 8. Regardless of the category of the performance characteristics, a larger S/N value corresponds to a better performance. Based on the analysis of the S/N ratio, the optimal combination for low porosity is obtained at 14 wt%/volume electrolyte concentration (level 1), 20 °c electrolyte temperature (level 4) and 18 volts voltage (level 2).

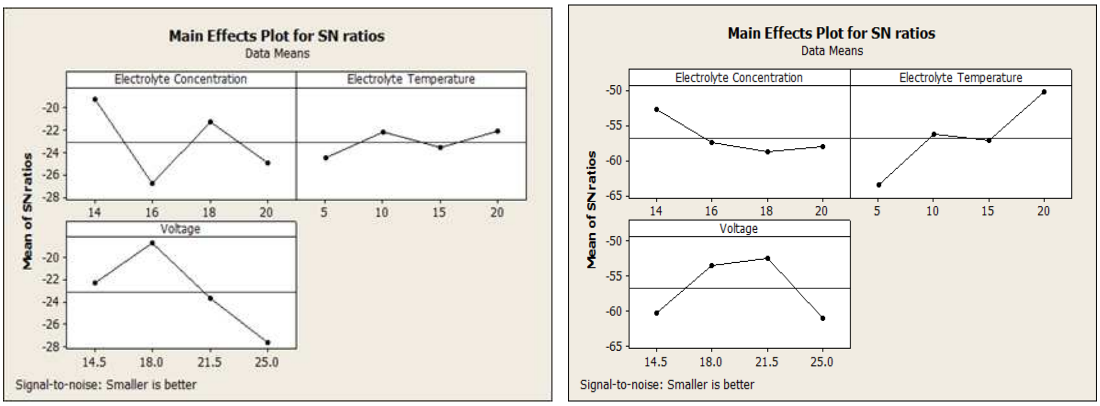
Table 7: S/N Ratio Values for Porosity by Factor Level

Level	Electrolyte Concentration	Temperature	Voltage
1	-52.62	-63.50	-60.16
2	-57.45	-56.15	-53.35
3	-58.79	-57.15	-52.41
4	-58.04	-50.10	-60.98
Delta	6.16	13.4	8.57
Rank	3	1	2

Table 8: S/N Ratio Values for Pore Density by Factor Level

Level	Electrolyte Concentration	Temperature	Voltage
1	-19.28	-24.47	-22.27
2	-26.77	-22.24	-18.74
3	-21.31	-23.58	-23.71
4	-25.01	-22.08	-27.65
Delta	7.49	2.39	8.91
Rank	2	3	1

Figure 2 shows the effect of process parameters on the porosity of anodic oxide films. Similarly from the analysis of the S/N ratio, the optimal combination for low pore density is obtained at 14 wt%/volume electrolyte concentration (level 1), 20 ºc electrolyte temperatures (level 4) and 21.5 volts voltage (level 3). Figure 2 (b) shows the effect of process parameters on the pore density.



(a) **(b)**

Figure 2: S/N Ratio Plot for (a) Porosity and (b) Pore Density

ANALYSIS OF VARIANCE (ANOVA)

ANOVA is a statistically based, objective decision-making tool for detecting any differences in the average performance of groups of items tested. ANOVA helps in formally testing the significance of all main factors and their interactions by comparing the mean square against an estimate of the experimental errors at specific confidence levels.

The P-value reports the significance level (suitable and unsuitable). Percent (%) is defined as the significance rate of the process parameters on the output responses. It can observed from Table 9 that the electrolyte concentration, electrolyte temperature and voltage affect the porosity by 38.38%, 4.27% and 44.83% respectively during the anodization of AA 6061 in sulphuric acid. Similarly from Table 10 it can be seen that electrolyte concentration, electrolyte temperature and voltage affects pore density by 10.42%, 40.36% and 26.76% respectively during the anodization of AA 6061 in sulphuric acid.

Table 9: ANOVA Results for Porosity

Source	Degrees of Freedom	Sum of Squares	Mean of Squares	F	P	% of Contribution
Electrolyte concentration	3	139.67	46.557	6.14	0.029	38.38
Electrolyte temperature	3	15.56	5.188	0.68	0.594	4.27
Voltage	3	163.15	54.383	7.17	0.021	44.83
Error	6	45.49	7.582			12.5
Total	**15**	**363.88**				

Table 10: ANOVA Results for Pore Density

Source	Degrees of Freedom	Sum of Squares	Mean of Squares	F	P	% of Contribution
Electrolyte concentration	3	93.33	31.11	0.93	0.482	10.42
Electrolyte temperature	3	361.26	120.42	3.6	0.08	40.36
Voltage	3	239.53	79.84	2.38	0.168	26.76
Error	6	200.87	33.48			22.44
Total	**15**	**894.99**				

Confirmation Test

The confirmation test is the final step in verifying the results obtained from Taguchi's design approach. The optimal conditions are set for the significant factors and experiments are run under specified anodizing conditions. The confirmation experiment is a crucial step and is highly recommended by Taguchi to verify the experimental results.

In this study, a confirmation experiment was conducted for low porosity and low pore density by utilizing the levels of the optimal process parameters. The porosity obtained at 14 wt%/volume electrolyte concentration (level 1), 20 °c electrolyte temperature (level 4) and 18 volts voltage (level 2) is 3.92%. Similarly, the pore density obtained at 14 wt%/volume electrolyte concentration (level 1), 20 °c electrolyte temperatures (level 4) and 21.5 volts voltage (level 3) is 120 pores/μm^2.

CONCLUSIONS

This study has discussed an application of the Taguchi method for investigating the effects of process parameters on the porosity and pore density during the anodization of AA 6061 in sulfuric acid. From the analysis of the results in the anodization process using the conceptual signal-to-noise (S/N) ratio approach, analysis of variance (ANOVA), and Taguchi's optimization method, the following can be concluded from the present study:

The optimal combination for low porosity is obtained at 14 wt%/volume electrolyte concentration (level 1), 20 °c electrolyte temperature (level 4) and 18 volts voltage (level 2).

The optimal combination for low pore density is obtained at 14 wt%/volume electrolyte concentration (level 1), 20 °c electrolyte temperatures (level 4) and 21.5 volts voltage (level 3).

Statistical results (at a 95% confidence level) shows that voltage is the significant factor affecting porosity and electrolyte temperature is the significant factor affecting pore density during the anodization of AA 6061 in sulphuric acid.

The porosity and pore density obtained after confirmation test are 3.92% and 120 pores / μm^2 respectively.

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