Investigation of Etchants for Etching Conditions of Aluminium

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Abstract
The purpose of the present work was to examine alternative etching conditions of aluminium. It has been investigated the effects of etching solution type, solution concentration on the etching behavior for aluminum. The measurements of depth of etch and etch rate values were measured by using 0-150 mm electronic digital caliper. Mitutoyo SJ-301 equipment was used for analyzing the surface of the aluminium. The effects of selected chemical etching parameters on depth of etch and surface finish quality were investigated. The best etching results were observed by using HCl solution but the surface quality with this solution had to be improved. Also it was concluded that etching solution and concentration have important effects on aluminium surface quality.

Keywords: surface treatments, selection of material processes, chemical reactions

1. Introduction

Aluminium alloys have various applications; used extensively in electrical transmission lines, coated mirrors, packages, toys, automotive, construction of aircraft and rockets (Çakir et al., 2007). The appearance and the serviceability of an aluminium product depend largely on surface treatments, which precede the actual finish (Terryn, 1994). Aluminium manufacturers use "surface pretreatment (surface preparation) techniques" for aluminium before surface coating by anodizing purification.
Chemical etching is a process that is performed with strong chemical solution, called "etchant". Alkaline etching of aluminum has been the traditional and commercial method of surface preparation for anodizing. Chemical etching can be carried out in a number of solutions but the simplest and cheapest form is alkaline solutions based on caustic soda (Çakir, 2008; Koroleva et al., 1999). Various studies were mainly focused on improving the alkaline-based etchants. Dash et al. (2007) have investigated the effect of temperature and alumina/caustic ratio on precipitation of boehmite in synthetic sodium aluminate liquor. Feliu and Bartolome (2007) have remarked that this type of etching solution often contains various additives, e.g. nitrites, fluorides, wetting agents etc., which modify the etching action.
Despite its extensive usage of alkaline-based etchants, there are drawbacks to the commercial process, such as controlling the concentration of sodium aluminate that composes by the reaction between the aluminum and caustic soda. Because of aluminium trihydrate production, etching quality decreases and waste disposal cannot be controlled (Pajunen, 2007). And on account of the different problems, connected with the price of caustics rising and landfill space diminishing, canalized scientists to invest different chemical etchants. Chambers (2000) has investigated the etching of aluminium alloys by ferric ion. The essence of his study was to show that aluminium can effectively be etched by a ferric compound alone in solution or preferably in an acidic solution. Similarly, Oh et al. (2007) have aimed to investigate the etching characteristics of high-purity aluminum in hydrochloric acid solutions. According to their study, the addition of sulfuric acid or ethylene glycol to the hydrochloric acid solution has caused to get more uniform etching tunnels. In addition, Allen and Almond (2004) have studied the characterization of aqueous ferric chloride etchants used in industrial photochemical machining. They mainly concerned to define standards for industrial etchants (that are not chemically pure) and methods by which they are analyzed and monitored. Among all these studies it has been noticed that the selection of efficient etchant in chemical etching of any material is probably the most important parameter.
In general, hydrochloric acid is used for the etching solution, but because of its high corrosiveness the size and distribution of etch pits are not uniform with the low density of them (Oh, 2007). In the present

study in order to improve these etchants, we have studied the effects of etching solutions and etchant concentrations. Depth of etch and etching rate values were measured. The quality of the etched samples was verified by "surface roughness" values obtained.

2. Experimental

The experimental study of chemical etching of aluminium was carried out in beaker, using immersion etching method. The chemical composition of selected aluminium was given in Table 1. The surface roughness of the material was 0.27 µm before the etching experiments. The thickness of specimen was 1 mm and it was cut at 45 mm x 70 mm dimensions.

Table 1. Chemical composition of aluminium

Chemical elements (%)									
Al	**Si**	**Fe**	**Cu**	**Mn**	**Mg**	**Zn**	**Ti**	**Cr**	**Others**
96,0	0,47	0,20	0,01	0,01	0,62	0,01	0,01	0,01	0,05

The experimental study was consisting of three steps: (i) degreasing, (ii) etching and (iii) cleaning. The first step consists of removing grease, oil, heavy oxides and other contaminations from the surface of the aluminium. The specimens were degreased by submerging them in an aqueous solution of sulphuric acid and chromic acid in concentrations of 15 % vol. and 5 % vol., respectively, for 10 min. at room temperature. Afterwards, the samples were dried at atmospheric conditions.
Four different acids (HCl, $HClO_4$, H_2SO_4 and CH_3COOH) were prepared at 15 vol. % with distilled water to investigate the acidic etchant parameter. The selected etching bath concentrations were 5, 10, 15 and 20 vol. % to investigate the etchant concentration. All chemicals were supplied by Merck and deionized water was used to prepare all the aqueous solutions.
After determination of the acid, it was observed the acid addition the etching bath ($FeCl_2$,) acid concentration (0.25, 0.5, 0.75 and 1 M). Also the effects of the etching temperature (room temperature, 40 ^{0}C, 50 ^{0}C and 60 ^{0}C) and etching time (5, 10, 15 and 20 min.) parameters were investigated. And in order to observe the effect of acid addition to the etching bath, four different acids were used (H_2SO_4, H_3PO_4, HCl, HNO_3).
After the etching process, the aluminium samples were cleaned in a cleaning bath, containing 30% nitric acid solution. This step was carried out to remove spots that occur because of the Cu, Mn and Si elements. The measurements of depth of etch and etch rate were carried out by 0-150 mm electronic digital caliper. Mitutoyo SJ-301 equipment was used for analyzing the surface of the aluminium by obtaining "surface roughness" values. For each etched specimen, surface roughness tests were repeated three times, and the averages of them were reported.

3. Results and discussion

Depth of etch is one of most important etching outputs in chemical etching of materials. Etch rate, in mm/surface/hour, is also an important parameter and is definitively determined by measuring the depth and the weight of the specimen, immersed to etching bath for a selected time. The ½ term at the numerator discloses the total etch per surface. Etch rate on an hourly basis is expressed by applying the hour fraction of the immersion time.

$$\text{Etch rate} = \frac{(\text{weight loss})(\text{thickness in mm.})(1/2)(60)}{(\text{original weight})(\text{minutes immersed})} \qquad (1)$$

Surface roughness presents the effectiveness of the chemical etching process when it is used for weight reduction purpose. There are many different roughness parameters in use, but R_a, arithmetic average of absolute values, is by far the most common (Cakır, 2008).

3.1. Effect of acidic bath

Four different acids (HCl, $HClO_4$, H_2SO_4 and CH_3COOH) were selected to investigate the effect of acidic etchants on aluminium etching properties. Experiments were performed at room temperature for 20 minutes. The depth of etch and etch rate values obtained were given in Figure 1. The highest depth of etch and etch rate values were obtained with 15 vol. % HCl concentrations, with other acids it was obtained less depth of etch and etching rate values. This is due to chemical activation of HCl.

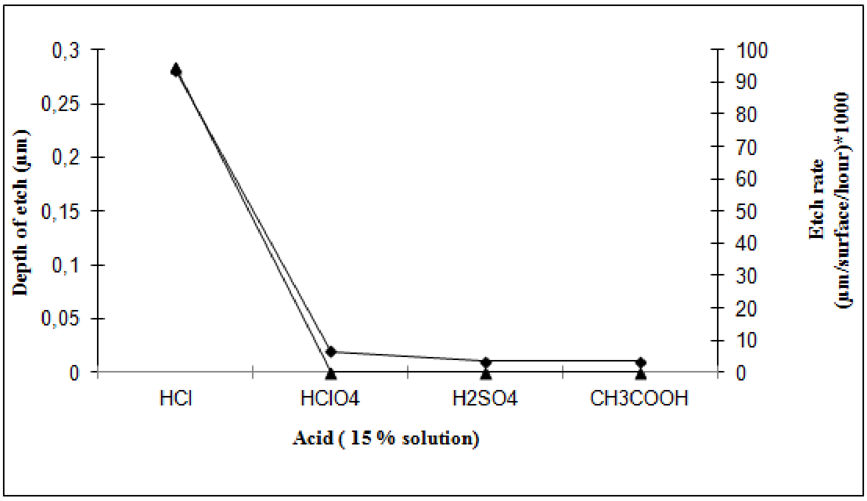

Figure 1. Etching properties at different acidic baths (♦depth of etch, ▲etching rate)

The effective chemical etchant would produce a higher etch rate (and also depth of etch) and smooth surface finish (Cakır, 2008). Figure 2 shows that 15 vol % HCl is not suitable for etching bath because of the high surface roughness values.

Acid amount is also an important factor related to high performance etching solution. In order to investigate the effect of acid amount, experiments were performed by using 5-10-15 vol. % HCl, $HClO_4$, H_2SO_4 and CH_3COOH solutions as etching bath. The effect of acidic bath concentration was investigated at 40 ^{0}C for 10 minutes. The results were given at Figure 3 and Figure 4.

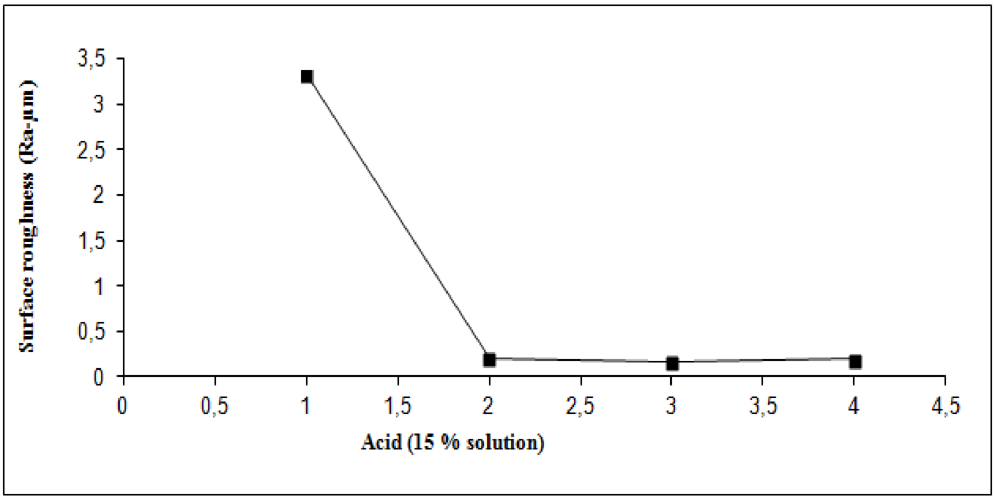

Figure 2. Effect of acid at etching bath on surface roughness (HCl)

Increasing the concentrations of $HClO_4$, H_2SO_4 and CH_3COOH acids as etching solution had no important effect on depth of etch and surface roughness. Unlikely, the presence of HCl in the etching medium significantly improved etching properties. Higher concentrations of HCl caused higher etching properties. However, surface quality has decreased at higher concentrations.

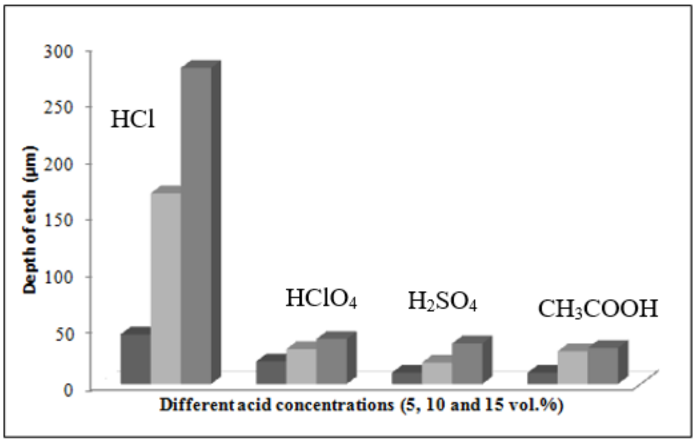

Figure 3. Etching properties at different etching bath concentrations (♦depth of etch, ▲etching rate)

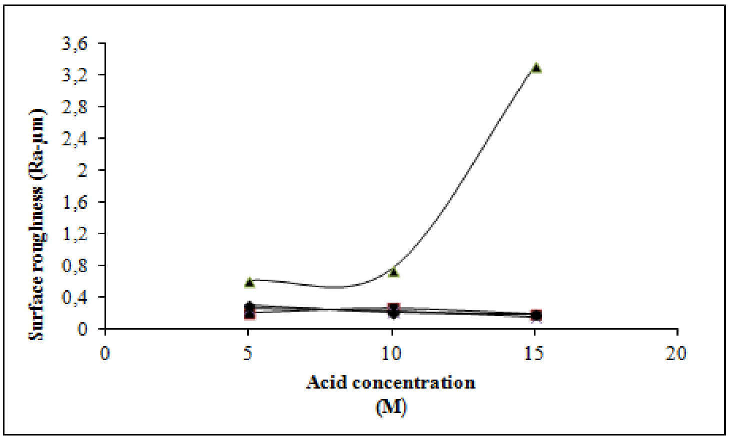

Figure 4. Effect of acid concentrations at etching bath on surface roughness (▲ HCl, ● $HClO_4$, ♦ H_2SO_4, ■ CH_3COOH)

3.2. Effect of etchants

Çakır (2008) and Chambers (2000) have concluded that iron based etchants are very suitable etchants for aluminium etching. In this study in order to investigate the effect of etchants on aluminium properties, 1 M of solutions of iron (III) nitrate, ammonium iron (III) sulphate, iron (III) chloride and iron (II) sulphate have been used. Etching experiments were performed at room temperature for 20 minutes. The depth of etch, etch rate, the surface roughness values can be seen at Figure 5-6.

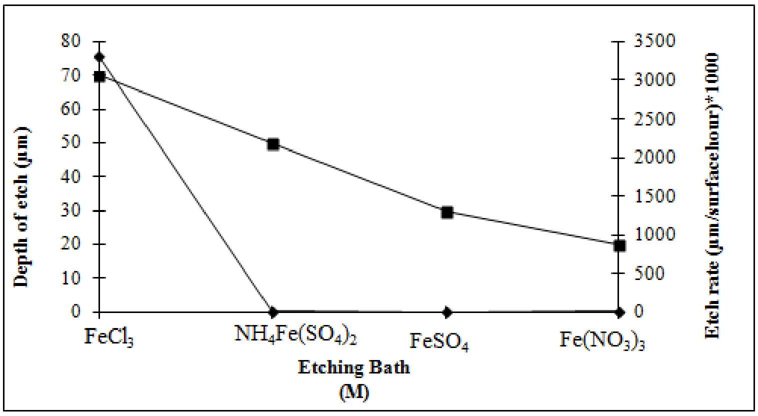

Figure 5. Effect of etchants on depth of etch, etch rate

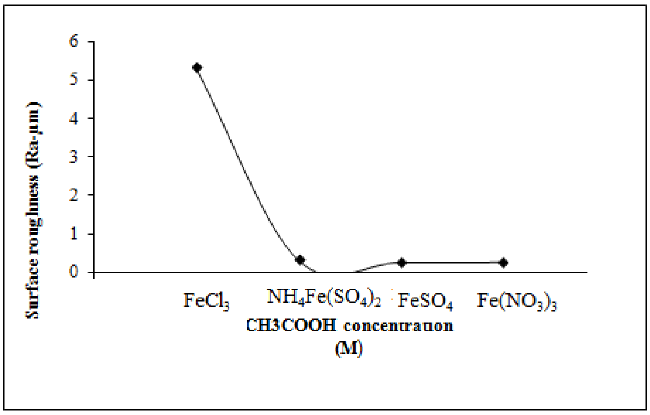

Figure 6. Effect of etchants on surface roughness

The highest depth of etch and etch rate values were observed for $FeCl_3$ solution. As aluminium was dissolved into solution, etchant was consumed and the by-products of ferrous chloride ($FeCl_2$) and aluminium chloride ($AlCl_3$) were generated, and could be written as follows:

$$3FeCl_3 + Al \longrightarrow 3FeCl_2 + AlCl_3 \qquad (2)$$

$NH_4Fe(SO_4)_2$ and $Fe(NO_3)_3$ solutions caused less etching rates compared to $FeCl_3$. No etching was observed by using $FeSO_4$ as an etchant in the bath. However, surface quality has decreased at high etch rates. So it was decided to investigate the effect of etching bath concentration on aluminium with $FeCl_3$ solution and to develop the surface roughness values.

3.3. Effect of etching bath concentration

Four different $FeCl_3$ concentration values (0.25, 0.5, 0.75 and 1 M) were selected to investigate the effect of bath concentration on aluminium etching properties. Experiments were performed at room temperature for 20 minutes. The depth of etch and etch rate values obtained were given in Figure 7. The influence of bath concentration on depth of etch was positive, depth of etch increased when higher $FeCl_3$ concentration was used. The highest depth of etch and etch rate values were obtained at 0.75 and 1 M concentrations, lower concentrations produced less depth of etch values. This is due to chemical activation of the etchant at high concentrations; the etchant becomes more active for etching.

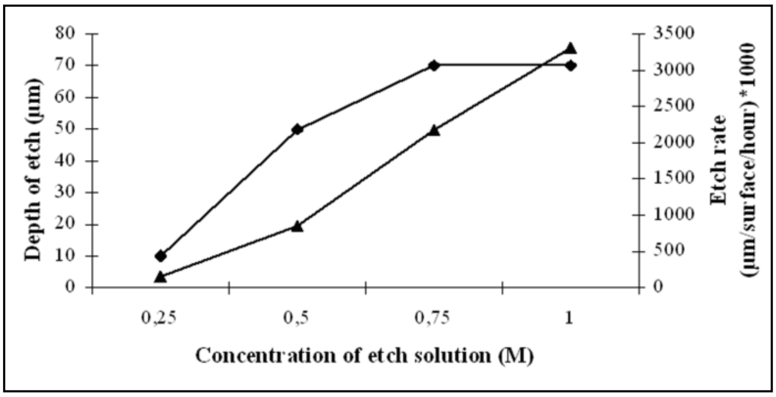

Figure 7. Etching properties at different bath concentrations (♦depth of etch, ▲etching rate)

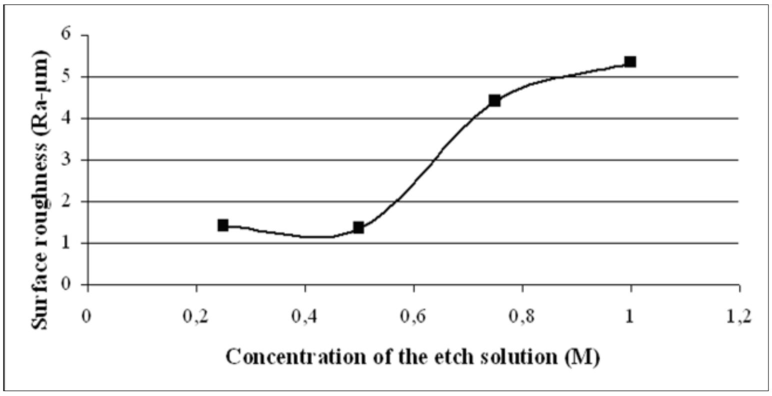

Figure 8. Effect of bath concentration on surface roughness

The aluminium specimens were tested using surface roughness method to obtain information about surface quality. The test results for all different etching bath concentrations were given in Figure 2. It was observed that surface finish quality was mainly affected by concentration of etch solution. In view of higher concentrations caused decreasing in surface quality, it was decided to investigate the effect of etching temperature and time on aluminium and to develop the etching properties.

3.3. Effects of etching temperature and time

The effect of etching temperature was investigated using $FeCl_3$ solution at 0.25 M etching bath concentration for 20 minutes etching period. These results were shown in Figure 9-10. Etch rate has increased by increasing temperature. Depth of etch was stable until 40 ^{0}C, and was increased in the range of 40-50 ^{0}C. Increasing temperature to 60 ^{0}C has caused no change at depth of etch. The highest depth of etch was obtained at 50 ^{0}C and 60 ^{0}C, lower etching temperatures has produced less depth of etch values. This is due to chemical activation of the etchant at high temperature; the etchant becomes more active for etching.

For determining surface finish quality, etching temperature is also an important factor. It was noticed that higher etching temperatures generally increase surface roughness values. Using higher etching temperature produced poor surface quality. The lowest surface roughness was obtained at room temperature and the highest was at 60 ◦C.

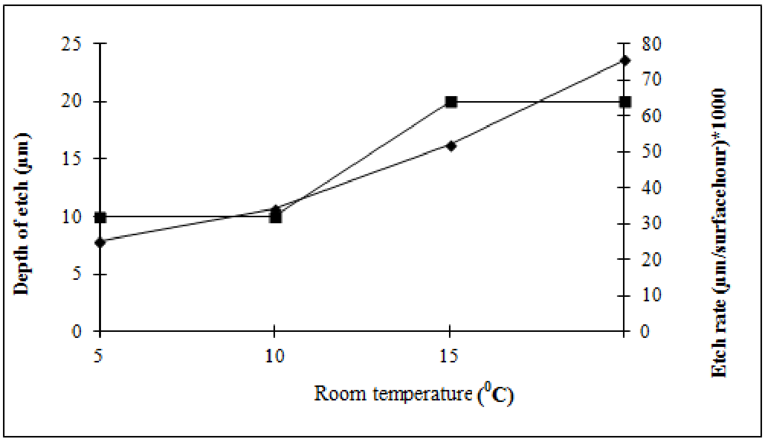

Figure 9. Effect of etching temperature on depth of etch, etch rate (after 20 min. etching time at 0.25 M etching bath concentration)

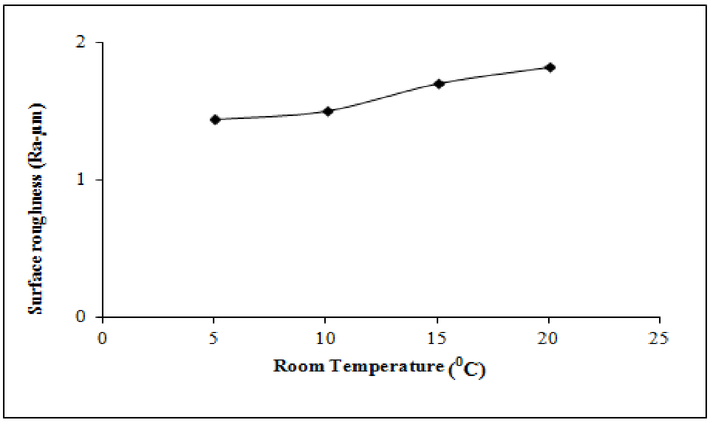

Figure 10. Effect of etching temperature surface roughness (after 20 min. etching time at 0.25 M etching bath concentration)

Etching time was also examined at 40 ^{0}C. As shown at Figure 11-12, it was observed that the depth of etch and etch rate increased with etching process continued and significantly highest etching properties were detected at 20 min.

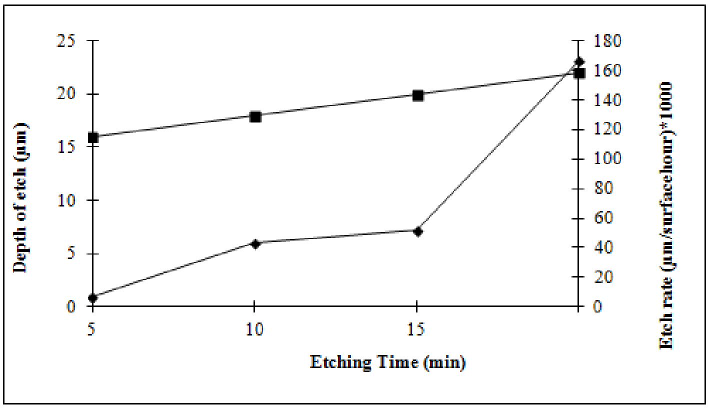

Figure 11. Effect of etching time on depth of etch, etch rate (at 40 ^{0}C and 0.25 M etching bath concentration)

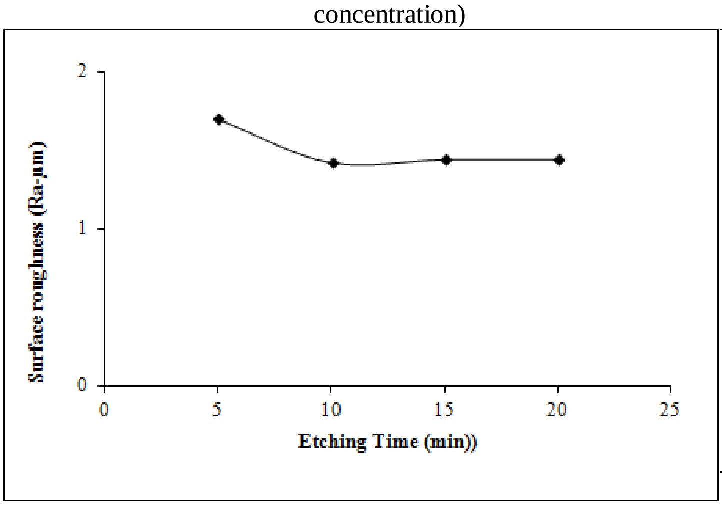

Figure 12. Effect of etching time on surface roughness. (at 40 ^{0}C and 0.25 M etching bath concentration)

Increasing etching time has decreased surface roughness, because chemical etching was not properly occurred in the first part of etching process (especially at first 5 minutes of etching). After this period, the etching of aluminium was more stable during 20 minutes.

3.4. Effect of acid addition

Acid addition is an important factor related to high performance etching solution. In order to investigate the effect of acid addition, experiments were performed by adding 50 vol. % of 0.25 M four different acid solutions to 0.25 M of $FeCl_3$. The effect of acid addition to etch solution was investigated at 40 ^{0}C for 10 minutes. The results were given at Figure 13.

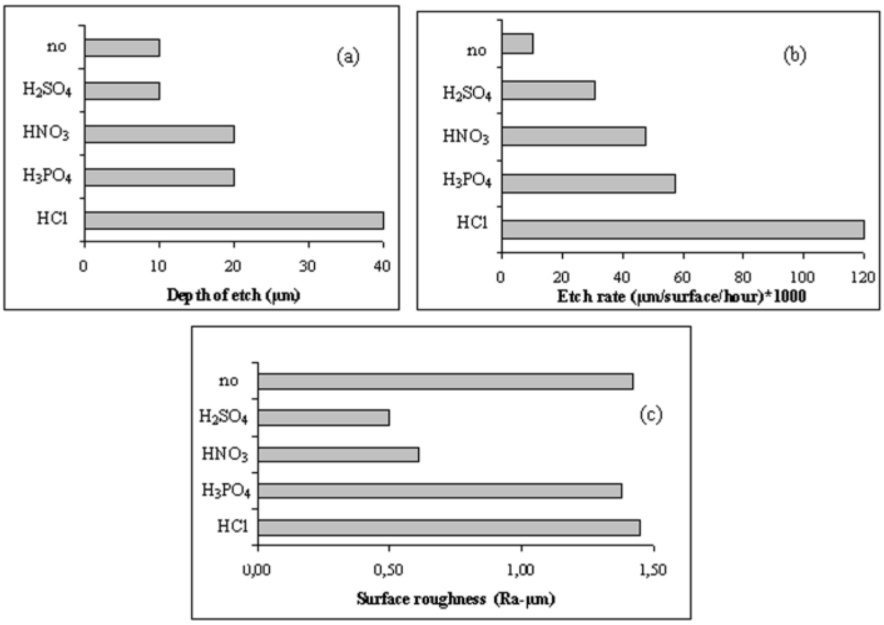

Figure 13. Effect of acid additives on depth of etch, etch rate and surface roughness

H_2SO_4 addition had no important effect on depth of etch and etch rate but has decreased surface roughness. Unlikely, the presence of HCl in the etching medium significantly improved etching properties. HNO_3 and H_3PO_4 caused lower etching performance than HCl, but higher than H_2SO_4. There has been no important effect for improvement of surface quality with HCl as it is seen at Figure 14a-c.

In addition, five different HCl amounts were used to investigate the effect of acid concentration at etching bath. The experiments were performed at 40 ^{0}C for 10 minutes and the obtained values were given at Table 2. Depth of etch and etch rate have increased by increasing HCl amount at etching bath. Higher concentrations of HCl caused higher etching properties. However, surface quality has decreased at higher concentrations. More HCl amounts (≥0.20) caused a constant quality at surface.

Table 2. Effect of HCl concentration on depth of etch, etch rate and surface roughness (at 40 ^{0}C and 10 min.)

HCl Concentration (M)	**Depth of etch (µm)**	**Etch rate (µm/surface/hour)*1000**	**Surface roughness (Ra-µm)**
0,1	10	28,09	0,67
0,15	20	42,27	0,865
0,2	20	72,82	1,41
0,25	40	120,00	1,42

Conclusions

The experimental investigation of chemical etching of EN AW- 6060 aluminium was completed by using $FeCl_3$ etchant at various concentrations, etching temperatures, etching times and acid additives. $FeCl_3$ was a very suitable etchant for aluminium etching among other experienced iron solutions. Depth of etch and etch rate were affected by the concentration of the etch solution, etching time, etching temperature and acid addition. Longer etching process, higher etching temperatures and HCl addition to the etch bath produced higher etching properties. Surface finish quality was also investigated. Lower bath concentration, lower bath temperature and higher etching time caused improvement at surface quality. Adding H_2SO_4 and HNO_3 improved surface roughness.

This study has also showed further research opportunities in the chemical etching of aluminium such as investigating some chemical additives to main etchant and examining other possible etchants.

Acknowledgments

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