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# STUDY ABOUT ALUMINIUM ETCHING

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ABSTRACT. Chemical etching is a micro-machining manufacturing process to produce micron-size components by applying of a chemical etching solution to remove unwanted part in the work-piece material. In this study aluminium was etched by different chemical agents (acid and base solution). The effects of selected chemical etching agents on depth of etch as well as the etch rate was investigated for aluminium.

KEYWORDS: etch rate, depth of etch, chemical etching, resist, developer, erosive agent.

## 1. INTRODUCTION

Chemical etching process has a long history and accepted one of the non-traditional machining processes. The method is widely applied to machine geometrically complex parts from thin and flat of any material. It is also used to reduce weight of the work-piece materials [3].

Aluminium and aluminium alloys have emerged as alternate materials in aerospace and in some chemical process industries. Due to their wide applications, they frequently come in contact with acid or bases during pickling, de-scaling, electrochemical etching and extensively used in many chemical process industries.

Phosphoric acid medium [4] is widely used for acid etching of aluminium. Even though dissolution rate of aluminium in phosphoric acid medium is lower, compared to the dissolution of the same in hydrochloric medium or sulphuric acid medium, it does corrodes aluminium and its alloys.

Due to its high electric conductivity, aluminium is used for conductors in microelectronics where it is often alloyed with copper in order to prevent electro migration, or with silicon in order to prevent the formation of aluminium- silicon alloys.

The formation of a very thin $Al_2O_3$ film makes it very inert in many substances. Therefore, aluminium etching agents requires at least compounds for dissolving $Al_2O_3$ as well as for etching aluminium.

Aluminium etching is highly exothermic and under-etching of the resist mask causes local heating (increased etch rate) and super-proportional under etching of the mask as a consequence if no agitation is performed.

## 2. MECHANISM OF THE CHEMICAL EROSION

The action of the chemical agent is due to the anodic dissolution of the processed metal. The chemistry between the erosive agent and the processed material depends on the material structure and the surface geometry. During the chemical etching takes place the following transformations:

- dissolution with different rates of each particle from the metal;
- dissolution of the particles from the materials surface.

In the polycrystalline structure of metals and alloys, metallic crystals have different orientations in the atomic net. Between the atomic metals exists different distances that influence the material erosion. The most intense erosion is in the zones where the inter-metallic bonds are weaker and the distance between metallic atoms are greater.

The action of the erosive agent is more intense at the material surface; the great dissolution rate is because of the presented impurities as well as the imperfections of the metallic net. The chemical etching of the metal depends on the dimensions of the marginal particles. If the dimensions between them are small, the inter-atomic bonds are stronger and the machining is more difficult.

The mechanism of chemical erosion is explained by the thermodynamic instability of metals and alloys.

In accordance with this theory the necessary conditions for a metal to be chemically etched is that simultaneously with the ionization reaction to take place a reduction reaction of other electrons acceptor than the ion of the respective metal.

The presence of some impurities accelerates the metal erosion. If the impurity with a more positive potential has a greater value of the over-voltage of hydrogen ions releasing, decreases the erosion rate of the metal.

Generally, etching starts after the dissolution by etching agents [9] of few nm $Al_2O_3$ present of every Al surface. For this reason the alkaline etching solutions preferentially dissolve $Al_2O_3$ where the resist is primarily developed, at regions with lower resist film thickness or below cleared structures with larger features (figure 1):

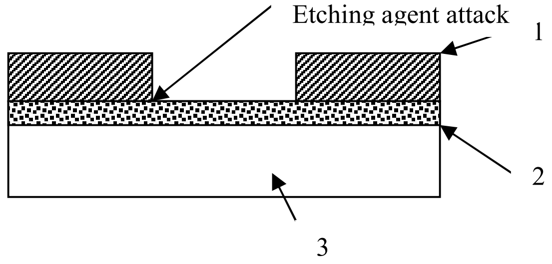

**Figure 1** Etching agent attack on the Al substrate
1- protective mask, 2-$Al_2O_3$ , 3- Al substrate

Chemical etching can be achieved by immersion in a bath with erosive agent or by spraying. The mechanism of metal erosion with a chemical agent is presented in the following figures [7]:

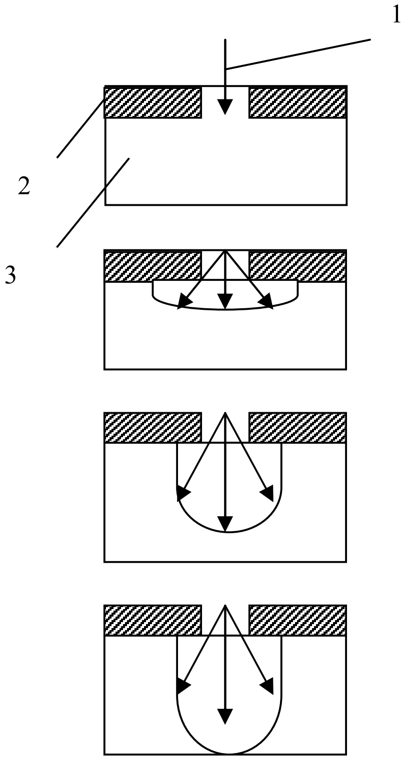

**Figure 2** Mechanism of the etching agent attack on the metal substrate
1- erosive agent; 2- protective mask; 3- work-piece

In figure 3 is presented the mechanism of chemical etching by spraying the erosive agent:

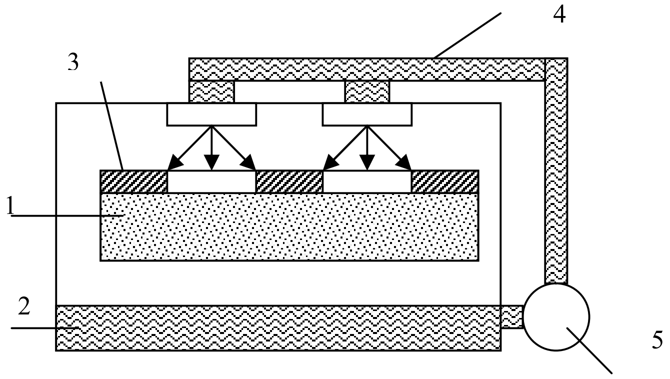

**Figure 3** Mechanism of the etching agent attack by spraying the work-piece surface
1-work-piece; 2-erosive agent; 3-mask; 4-distribution pipe; 5-pump

## 3. ALUMINUM ETCHING SOLUTIONS

### a) Alkaline solutions

The most applied etching solutions for aluminium and its alloys were alkaline solutions: caustic soda and NaOH. The chemical process that takes place is:

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2 \qquad (1)$$

The main drawbacks of this solution is the decreasing of the etching rate with the increasing of the aluminum concentration resulting a thin film of $Al_2O_3$ on the Al surface, that must to be periodically removed for a continuous machining.

The presence of the surface oxide film, $Al_2O_3$, should be considered in studying the erosion mechanism of aluminium in alkaline solution. The anodic dissolution reaction in the presence of the oxide film can be classified into a direct metal dissolution reaction by the movement of aluminium ions through the film and an indirect dissolution reaction by consecutive film formation and dissolution [6].

It is generally accepted [8] that the film formation proceeds electrochemically by the incorporation of the hydroxide ions into the film and migration through the film towards the aluminum interface in the presence of a thick film on the surface of aluminum:

$$Al + 3HO^- \rightarrow Al(OH)_3 + 3e^- \qquad (2)$$

The aluminum hydroxide film formed will be dissolved chemically by $HO^-$ attack at the film interface:

$$Al(OH)_3 + HO^- \rightarrow Al(OH)^-_4 + 3e^- \qquad (3)$$

The electrons produced by partial anodic reaction will be consumed immediately by such partial cathodic reaction as oxygen reduction:

$$3/4O_2 + 3/2H_2O + 3e^- \rightarrow 3HO^- \qquad (4)$$

And the water reduction reaction:

$$3H_2O + 3e^- \rightarrow 3/2\ H_2 + 3HO^- \qquad (5)$$

The short-circuited erosion reaction of pure aluminium in alkaline solution can be represented as:

$$Al + HO^- + 3/4O_2 + 3/2H_2O \rightarrow Al(OH)^-_4 \qquad (6)$$

Where $Al(OH)^-_4$ represents the aluminate ions.
A partial anodic dissolution reaction of aluminium in alkaline solution can be obtained by combining electrochemical film formation and chemical film dissolution:

$$Al + 4HO^- \rightarrow Al(OH)^-_4 \qquad (7)$$

Due to the elements from aluminum alloys the obtained results for chemical etching were not always satisfactory. Cu, Fe, Zn from aluminum alloys achieves galvanic couple with aluminum during the chemical erosion [1] and the obtained surfaces will have a great roughness. To obtain a surface with a small roughness is added sulfur compounds ($Na_2SO_3$, $NaHSO_3$) that precipitate cooper, zinc and the other alloyed compounds.
In table 1 are given some of the alkaline solution for chemical etching of aluminum:

**Table 1** Alkaline etching agents for aluminum

| Etching compounds | Concentration [g/l] | Observations |
|---|---|---|
| NaOH<br>Al | 80-180<br>8-60 | Poor quality of the processed surface |
| NaOH<br>Al<br>$Na_2SO_3$ | 78-170<br>20-75<br>6-200 | |
| NaOH<br>Sodium metaaluminat<br>$Na_2SO_3$<br>Sodium gluconat | 180-270<br>20-75<br>90-180<br>0,3-0,6 | T= 66-71$^0$C |
| NaOH<br>Al<br>$(C_2H_5OH)_3N$ | 100-40<br>10-60<br>45-90 | For obtaining of a surface with great smoothness |

Aluminum machining by chemical erosion releases a great quantity of heat (388 cal/g). The erosion rate is controlled by the temperature and the concentration of NaOH. By doubling the NaOH concentration the reaction rate increases from 0,002 mm/min to 0,003 mm/min.
Reaction 1 takes place with a smaller rate with the decreasing of NaOH concentration and the increasing of aluminum concentration. For a constant etching rate is necessary that the alkaline solution [5] to be continuously added during the etching process.
The used solutions of etching agents by cooling achieves $Al_2O_3$ , $Al(OH)_3$ and NaOH:

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH \qquad (8)$$

$$NaAlO_2 + 4H_2O \rightarrow Al_2O_3 + 3H_2O \qquad (9)$$

These reactions permit to recover the sodium hydroxide and to separate the aluminum.

**b) Acid solutions**

Etching agents with HCl [4] permits the applying of some protective masks with a low cost. The high cost of the machining equipments reduces the processes that use acid etching agents to the aluminum machining.
In acid solutions takes place the reactions:

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2 \qquad (10)$$

A part from the acid can be recovered:

$$AlCl_3 + 3HOH \rightarrow 3HCl + Al(OH)_3 \qquad (11)$$

Among the acid etching agents for aluminum etching were mixtures of HCl, $H_3PO_4$, $Na_2Cr_2O_7$ , $HNO_3$, $CH_3COOH$ and $FeCl_3$.
The acid etching solutions are given in table 2:

**Table 2** Acid etching agents for aluminum

| Etching compounds | Concentration [g/l] |
|---|---|
| HCl<br>$AlCl_3$ | 2-3<br>50-80 |
| HF<br>HCl<br>$HNO_3$ | 22-75<br>26-42<br>111-300 |
| $H_2CrO_4$<br>$H_2SO_4$ | 30-53<br>165-225 |

For aluminium etching was also used a mixture of $HNO_3$, HCl and HF acids. The reactions in this case are:

$$2Al + 6HF \rightarrow 2AlF_3 + 3H_2 \qquad (12)$$

$$8Al + 6HNO_3 + 24HF \rightarrow 8AlF_3 + 3N_2O + 15H_2O \qquad (13)$$

$$Al + HNO_3 + H_2O \rightarrow H_3AlO_3 + NO \tag{14}$$

$$Al + 3HCl + HNO_3 \rightarrow AlCl_3 + NO + 2H_2O \tag{15}$$

$$8Al + 24HF + 6HNO_3 \rightarrow 8AlF_3 + 3NH_4NO_3 + 9H_2O \tag{16}$$

$$2H_3AlO_3 + AlF_3 \rightarrow 3AlOF + 3H_2O \tag{17}$$

$$CH_3COOH + 2H_2 \rightarrow CH_3CHO + H_2O \tag{18}$$

The aluminium removed during the processes will form a precipitate of oxifluoride of aluminium (AlOF) that will be separated through filtration.
Among the etching acids used at the machining by chemical erosion of aluminium were mixtures of HCl, $K_2Cr_2O_7$, $HNO_3$, $CH_3COOH$, $FeCl_3$.

## 4. EXPERIMENTAL METHOD

The material used for this work was aluminium, samples rods had 22 mm width and 24 mm length, erosion time=10 min.
Aluminium etching is highly exothermic an under etching of the resist mask causes local heating (increased etch rate) and super-proportional under-etching of the mask as a consequence, if no agitation is performed.
Each aluminium plate was etched in alkaline solutions NaOH, and acid solutions HCl and $H_3PO_4$ with concentrations 0,01; 0,25; 0,5; 0,75; 1M. Experiments were carried out using a calibrated thermostat at temperature 30$^0$C.
Etch rate was calculated using equation:

$$Etch\ rate = \frac{\Delta d}{t} \quad [\text{Å/min}] \tag{19}$$

$\Delta d = d_0 - d_1$ thickness change after etch [Å]
$t$ – etch time [min.]
$d_0$ – thickness before etch [µm]
$d_1$ – thickness after etch [ µm]

## 5. RESULTS AND DISCUSSION

The effect of acid and alkaline chemical etching solutions on the depth of etch as well as the etch rate were investigated.
The etch rate was calculated for aluminum etching in NaOH, $H_3PO_4$ and HCl solutions and the obtained results are presented in tables 2 ,3 and 4:

**Table 3** Etch rate of aluminum in HCl

| C (M) | 0,01 | 0,25 | 0,5 | 0,75 | 1 |
|---|---|---|---|---|---|
| Etch rate ($10^3$ Å/min) | 0,13 | 0,23 | 0,93 | 1,66 | 2,09 |
| | 0,25 | 0,27 | 0,85 | 1,73 | 2,13 |
| | 0,18 | 0,35 | 0,89 | 1,78 | 2,23 |
| | 0,27 | 0,38 | 0,94 | 1,84 | 2,40 |
| | 0,32 | 0,35 | 0,92 | 1,96 | 2,53 |

**Table 4** Etch rate of aluminum in $H_3PO_4$

| C(M) | 0,01 | 0,25 | 0,5 | 0,75 | 1 |
|---|---|---|---|---|---|
| Etch rate ($10^3$ Å/min) | 0,32 | 1,39 | 2,60 | 4,26 | 5,50 |
| | 0.36 | 1.17 | 2.65 | 4.30 | 7.54 |
| | 0.37 | 1.77 | 2.40 | 4.18 | 6.72 |
| | 0.40 | 1.56 | 2.80 | 4.90 | 10.46 |
| | 0.46 | 1.82 | 2.75 | 4.60 | 14.72 |

In figures 4 and 5 are presented the etch rates for aluminium in acid solutions ( HCl and $H_3PO_4$):

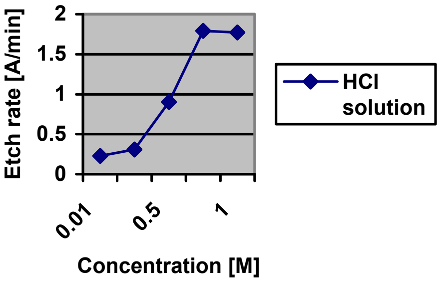

**Figure 4** Etch rate of aluminium in HCl solution

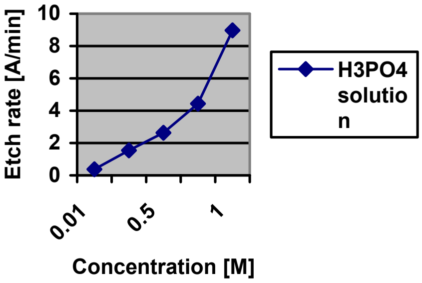

**Figure 5** Etch rate of aluminium in $H_3PO_4$ solution

**Table 5** Etch rate of aluminum in NaOH

| C(M) | 0,01 | 0.25 | 0,5 | 0,75 | 1 |
|---|---|---|---|---|---|
| Etch rate ($10^3$ Å/min) | 2,72 | 3,06 | 4,62 | 5,16 | 6,58 |
| | 2.35 | 2.65 | 4.76 | 5.20 | 6.35 |
| | 2,47 | 3,25 | 4,91 | 5,36 | 6,72 |
| | 2,56 | 3,42 | 4,87 | 5,42 | 6,64 |
| | 2,63 | 3,58 | 4,84 | 5,62 | 6,80 |

The etch rate of aluminium in NaOH solution is presented in figure 6:

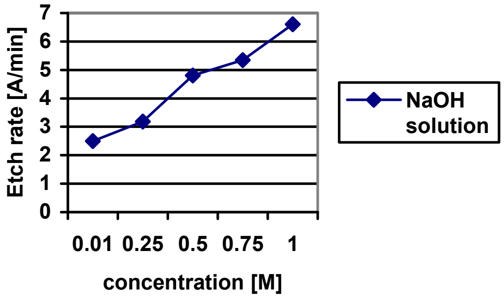

**Figure 6** Etch rate of aluminium in NaOH solution

The results indicate the increase of the etch rate with an increase of the concentration of the etching agents. The best etch rates were obtained in an alkaline solution ( NaOH ).

In figure 7 is presented a comparative analysis between etch rates obtained in acid and alkaline solutions:

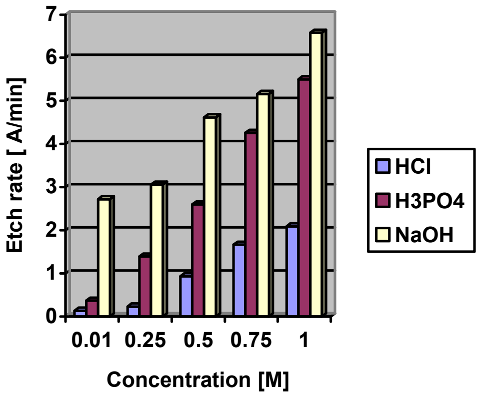

**Figure 7** Dependence of the etch rate values on the concentration of the erosive solution

## 6.CONCLUSIONS

- Aluminium alloy undergoes chemical erosion both in acid medium and in sodium hydroxide medium.
- The etching rate increases with the increasing of the concentration of acid medium as well as sodium hydroxide medium.
- The chemical erosion of aluminium alloy is more severe in hydroxide medium than in acid solutions.
- The etching rate in hydroxide solution is greater because of the anodic dissolution obtained by combining electrochemical film formation and chemical dissolution.
- Because of the alloys elements form the structure of aluminium alloys, the obtained results at the machining by chemical etching of aluminium with sodium hydroxide (NaOH) were not always satisfactory.
- The erosion rate of aluminium decreases with the decreasing of NaOH concentration and the increasing of aluminium concentration. For a constant etching rate is necessary that the alkaline solution [5] to be continuously during the etching process.

Cu, Zn, Fe elements form aluminium alloys makes galvanic couples with aluminium during chemical erosion, that generates the obtaining of some surfaces with great roughness. The surface roughness can be decreased by adding of some compounds with S: $Na_2SO_3$, $NaHSO_3$ that precipitates copper, zinc and the others elements from aluminium alloy.

- The action of the erosive agent is more intense at the material surface, the presented impurities and the imperfections in the metallic net influences the dissolution rate which is greater.
- Because of the $Al_2O_3$ film, aluminium etching requires strong chemical agents not only for dissolving the film but also for etching aluminium.
- The high cost of the machining equipments reduces the processes that use acid etching agents to the aluminum machining.

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