CHEMICAL ETCHING OF TITANIUM

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ABSTRACT
Chemical etching is a non-conventional process that permits to manufacture without distortion parts using thin metal. Titanium, chemical etched has many applications in medical, aerospace and defense industry. The physical properties of titanium, or any metal, are not affected by chemical etching and it has the advantage of a burr-free and stress-free process.

KEYWORDS: chemical etching, titanium, mask, erosion

1. INTRODUCTION
Titanium etching is a precise, economical and very efficient process with many applications range from medical device needing biocompatibility characteristics to aircraft applications that need an alloy that has superior strength and light weight. The selection of the chemical agent has an important influence on the finishing degree of the surface that will be processed. An ideal erosive agent uniformly removes the metal with a constant speed, obtaining a surface with roughness similar to that’s obtained by mechanical processing.

The surface’s roughness depends on the material’s quality that will be processed. If the processing depth is great, the influence isn’t important.

By chemical processing of different materials resulted surfaces with different roughness.

The surface’s roughness chemically processed is also influenced by the material’s structure; if it’s particles are small and uniform the surface will be proper finished. In the case of polycrystalline structure of metals and alloys the component particles could have different orientations in the metallic network. Areas characterized by a great distance between particles will be the most affected by the chemical attack. The alloying elements have an important influence; noble metals determine a surface improper finished.

In the following table is presented the finishing’s degree for some surfaces (µm) for different materials:

Table 1 Finishing’s degree of the surface obtained by chemical erosion

<table>
<thead>
<tr>
<th>Material</th>
<th>Shape</th>
<th>Finishing’s degree of surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum alloys</td>
<td>Plate</td>
<td>2-3,8</td>
</tr>
<tr>
<td></td>
<td>Molded</td>
<td>3,8-7,6</td>
</tr>
<tr>
<td>Magnesium alloys</td>
<td>Molded</td>
<td>0,75-1,4</td>
</tr>
<tr>
<td></td>
<td>Plate</td>
<td>0,75-1,5</td>
</tr>
<tr>
<td>Steel alloys</td>
<td>Plate</td>
<td>0,75-1,5</td>
</tr>
<tr>
<td>Nickel alloys</td>
<td>Plate</td>
<td>0,75-1</td>
</tr>
<tr>
<td>Titanium alloys</td>
<td>Plate</td>
<td>0,2-0,8</td>
</tr>
<tr>
<td></td>
<td>Molded</td>
<td>0,75-1,5</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Plate</td>
<td>1,5-3,3</td>
</tr>
</tbody>
</table>

At the processing by chemical erosion of the titanium alloys good results for the finished surface were obtained by using of hydrofluoric acid as erosive agent. The mixture hydrofluoric acid- chromic acid in spite of the great processing speed, is very aggressive for the protector material (mask). An undesired effect on the quality of the processed surface has the released hydrogen during the chemical reactions. A great quantity of hydrogen released in bubbles provokes parallel traces on the material’s surface.

For obtaining of good results by chemical erosion, from surface’s finishing point of view it is better that the pieces to undergo a thermic treatment before the processing.

Corrosion tests have demonstrated that the materials processed by chemical erosion are less affected by corrosion than materials mechanically processed.
2. TITANIUM PROCESSING BY CHEMICAL EROSION

The most frequent mixtures used at the titanium processing by chemical erosion were from hydrofluoric acid and chromic one’s or mixture of nitric acid and hydrofluoric acid. Chromic acid is less more used because of it’s high cost and of the problems that appear with the environment pollution. By chemical processing of titanium and it’s alloys with hydrofluoric acid takes place the reaction:

\[
6HF + Ti \rightarrow H_2TiF_6 + 2H_2\quad [1]
\]

Meanwhile between hydrofluoric acid and chromic acid the reaction is:

\[
3Ti + 30HF + 4CrO_3 \rightarrow 3H_2TiF_6 + 4CrF_3 + 12H_2O\quad [2]
\]

Because of the difficulties that appears at the using of chromic acid by formation of some aggressive compounds, in the acid mixture are introduced other oxidant agents as nitric acid when the reaction is:

\[
Ti + 6HF + 4HNO_3 \rightarrow H_2TiF_6 + 4NO_2 + 4H_2O\quad [3]
\]

The disadvantage of formation of nitric oxides in this case can be removed by adding urea in the mixture, that will reacts with nitric oxides. Oxidant agents presented in the erosive mixture favorable influenced the finishing degree of the surface. At the processing by chemical erosion of the titanium alloys in comparison with processing of aluminum alloys with the same method, is necessary to modify the concentration of the erosive solution depending on the processed material. At the titanium dissolution in hydrofluoric acid is released a great quantity of heat, 6338 cal/g. Because of the strong exothermic reaction, the erosion bath have to be permanently cooled to assure a proper reaction speed. The work temperature mustn’t to be greater than 55°C. In contrary case are released many nitric oxides that leads to the decreasing of the nitric acid from the erosive bath.

3. CHEMICAL EROSION’S MECHANISM OF TITANIUM

The process have a few steps:

1) Removing of the oxide layer from the surface: The titanium sheet is etched with an etching agent to remove the oxide layer and it is rinsed in water.

2) Covering the titanium’s surface with a protective macromolecular material: the protective material called mask can be an acrylic resin, a thermoplastic resin or a thermosetting resin which are resistant to the erosive agent.

3) Cutting the mask after a desired pattern: The protective material is removed with a cutting tool or a cutting machines after a certain pattern.

4) Chemical erosion (etching): titanium from the uncovered areas is etched with an erosive agent: hydrofluoric acid, ammonium, hydrogen fluoride, sulfuric acid and/or oxalic acid. The process consists from dipping the sheet in the etching agent and then rinsing with water.

5) Surface’s cleaning: after the achieving of the desired etching depth, the protective material is removed and the titanium sheet is cleaned. These steps are presented in fig. 1:

![Fig. 1 Mechanism of titanium chemical erosion](image-url)
4. PHOTO-CHEMICAL ETCHING OF TITANIUM

Photo-chemical etching is an application of chemical erosion applied for corrosion-resistant and biocompatible metals such as titanium, niobium, tungsten.

The process has the following steps:

1) Drawing and sketching: titanium sheet is covered with a photo-sensible material called photo-resist and a CAD and laser plotting system generate an exact image of the part on a set of photographic films that may contain from one to several thousands exact images.

2. Exposure to UV light: by a photo-chemical mechanism under exposure to an UV source the photographic film transfers part images on both sides of the sheet coated with photo-resist.

3) Chemical etching: the sheet is sprayed with a heated etching solution that dissolves metal not covered by photo-resist and the masked parts remain.

The photo-chemical etching is represented in figure 2:

1) Partially etched metal

2) Under-etched metal showing nominal dimensions

3) The metal has been etched to the nominal dimensions

Fig.2 Steps of photo-chemical etching

5. ADVANTAGES OF THE PROCESS

Processing by chemical erosion has many advantages toward other non-conventional processing:

a. Small roughness: work-pieces obtained by chemical erosion haven’t scratches that appears because of the transfer object (tool) in the mechanical process. A great advantage is the absence of the cutting forces.

A most frequent application of chemical erosion is finishing by material’s removing from pieces with thin walls mechanically obtained.

In the case of titanium, a hard material, is very useful a combined processing mechanical and chemical. The obtaining of some structure from titanium with thin walls is very difficult to achieve. The cutting forces that appears at the final processing can be greater than that’s supported by the material so will appears some local deformations and imprecision in processing.

b. Processing of hard materials: The utilization of different chemical agents permits the processing of some hard alloys and metals that were difficult to be mechanically processed. That’s fact permits the utilization of titanium and beryllium alloys especially in aeronautic industry. These type of alloys are difficult to be mechanically processed because of the very great cutting forces and high processing speeds.

Titanium is one of the metals that by forging, casting or extrusion retains oxygen or nitrogen at the surface. This surface known as “α” case is very hard and difficult to be processed. By piece’s processing appears a very high wear of the transfer object (tool) which can be avoided by using of erosive agents.

One of the technologies of chemical erosion that can be applied at the titanium alloys is chemical stamping that’s permit the obtaining of some continuous and smooth edges.

c. Smooth surfaces: For many materials as titanium, aluminum, steel alloys at the processing by chemical erosion is obtained a very smooth surface. An adequate erosive agent permits the obtaining of a roughness between 0,85-2,5 µm that doesn’t require a supplementary polishing. This fact reduces significantly the production expenses in comparison with that’s necessary at the mechanically processing. In the case of
Titanium alloys by chemical erosion can be achieved a surface's roughness of 0.25 µm. For obtaining of a very smooth surface it is necessary that before it's attack with erosive agent the surface to be checked to remove the eventually defects that are amplified by chemical erosion.

d) Reducing of the components number: by using of chemical erosion at an assembly obtaining are reduced the number of required tools. Many times an adequate assembly reduces significantly the necessary tools reducing in the same time the expenses for it’s maintaining. By reducing the components number from an assembly are reduced also the errors and the controlling time. By reducing the components number the assembly will be slighter and the time for dimensional control, smaller.

5. CONCLUSIONS

By chemical etching can be achieved intricate designs, parts using thin metal can be manufactured without distortion. The physical properties of titanium are not affected by chemical etching. It is essentially a burr-free and stress-free process.

Titanium etching has many applications in medical and aerospace industry, ranging from medical parts needing biocompatibility characteristics to aircraft applications that need an alloy that has superior strength and is also light weight.

REFERENCES


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