ABSTRACT
Chemical milling is used to establish intricate structural feature which can not be easily obtained by mechanical methods on titanium alloys parts. The goal of chemical milling is to achieve defined precision in structural features with good surface finishing and low hydrogen content.
The chemicals involved in the process include hydrofluoric acid, nitric acid and surface tension reducing agent. The chemistry in the chemical milling of titanium alloys is described.
Process control is also described.
Factors affect the result of the chem mill process are; type of Ti alloys, fabrication methods, geometry, racking, movement of parts, acid/Ti concentrations/ratio, solution temperature, mixing & operator.

INTRODUCTION
Titanium alloys is used in the aerospace industries due to its light weight, heat resistance characteristics, and strength. Chemical milling is used to shape the parts to meet detailed structural design which is not feasible by mechanical methods. Due to the unique characteristics of hydrofluoric acid, it is used to chem mill titanium alloys. Because of the local concentration of hydrogen gas during chem mill process is high; hydrogen content in the post chem mill parts can cause the embrittlement of the parts. In order to remediate the effect of hydrogen, it is necessary to reduce/remove hydrogen in situ and nitric acid is used to serve that purpose. If the nitric acid concentration is too high, it will result in a slow etch rate, rough surface finishing, channeling, pitting and striations. On the other hand, if HF is high, it will result in a fast etch rate, dishing, and uneven etch. If the dissolved titanium concentration in the solution is high, channeling and ridging will occur. If the Solution temperature too low, it will result in a slow etch rate, uneven etch and rough surface. On the other hand, if the solution temperature is too high, it will have a fast etch rate, dishing, uneven etch and excess nitrogen dioxide forming (orange-brown gas) which can attribute to acid rain when contact with moisture.
Chemical milling is a dynamic process and parts racking is important. In most cases, the parts are racked and submerged in the chem mill solution without any movement or minimal agitation of the solution. But for some intricate parts, it is necessary to have a devise which will provide one-to-two axis movement of the parts in the solution. Depending on the methods of fabrication of the titanium alloy parts, different types of chem mill solutions with different concentration of hydrofluoric acid and nitric acid are used. The ingredients in the tank require frequent analysis and adjustment. The total free acid concentration is determined by simple acid/base titration after precipitation of the interference from the dissolved titanium metal ions. Total fluoride and nitrate is determined with the use of ion chromatography (IC). The total amount of dissolved titanium
metal ion is determined spectrophotometrically after complexing the titanium metal ion with hydrogen peroxide in the presence of sulfuric acid and phosphoric acid. Statistical Process Control (SPC) is established and the data collected was used to assist in maintenance of all chem mill solution.

CONCLUSION
Although past history has shown that chemical milling of titanium alloys is a versatile method used in providing detailed features on the parts quite readily. It is beyond doubt that it is still, to a certain degree, an art of fabrication. With careful analyses, data collection and processing, it is possible to further understand the process and put the whole process under reasonable control.

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Ducommun, Inc.

- Publicly Traded (NYSE: DCO)
- Oldest Company in the State of California; Founded in 1849
- Three Business Units
  - Ducommun AeroStructures (DAS)
  - Ducommun Technologies (DTI)
  - Miltec
- 2007 Combined Sales $367M
- $1 B Sales in 2012
Your AeroStructures partner for the future
DAS Fundamentals

- Company Headquarters – Gardena, CA
- 2007 Annual Sales > $215m
- Centers of Excellence:
  - Gardena, California
  - Monrovia, California
  - Orange, California
  - El Mirage, California
  - Parsons, Kansas
  - Guaymas, Mexico
DAS Centers of Excellence

- More than 1m sq. ft.
- 6 facilities
- 1000+ employees

Gardena, California
Monrovia, California
Orange, California
Parsons, Kansas
El Mirage, California
Guaymas, Mexico
Center of Excellence – Chem Milling and vertically integrated processes
El Mirage, CA

70,000 sq. ft.
El Mirage, California

- Aluminum Chem Milling
  5 Tanks – up to 24 ft deep
- Titanium Chem milling
  9 Tanks – up to 15 ft deep
- Steel Chem milling
  10 Tanks – up to 6 ft deep
Size: 5,000 gal to 50,000 gal
Chemical Milling

Titanium Alloys
Chemical milling is a milling process by the use of chemicals to achieve intricate structural features which may not be easily obtained by mechanical milling.
• Cleaning
• Masking
• Scribing
• Line sealing
• Chem Milling
• Benching
Spray masking an engine duct for the JSF fighter aircraft.
F-16 F-110 engine waffle duct in the etchant line.
F-16 F-110 engine waffle duct in the etchant line
Titanium part that has been descaled and being checked to verify scale removal
Goals

- Good surface finishing
- Uniform metal removal
- Well-defined etch line
- Low hydrogen pickup
- Low hydrogen content
- Good physical strength
REACTIONS IN TITANIUM CHEMICAL MILLING PROCESS
Chemicals involved in this process are:

HF, Hydrofluoric acid
HNO₃, Nitric acid
Dissolved titanium
Surfactants
Water
During the chem mill process, titanium metal reacts with warm aqueous hydrofluoric acid solution to form soluble titanium hexafluoride and hydrogen gas and heat.

\[ \text{Ti} + 6 \text{HF} \rightarrow \text{TiF}_4 \cdot 2\text{HF} + 2\text{H}_2 \uparrow + \Delta \]

titanium hexafluoride
Titanium alloys have strong tendency to adsorb hydrogen gas and render the chem milled parts brittle. In order to remediate the hydrogen embrittlement of titanium during chem mill, nitric acid is added in the solution to remove the hydrogen gas as soon as it is formed.

\[ 2 \text{HNO}_3 + \text{H}_2 \uparrow \rightarrow 2 \text{H}_2\text{O} + 2 \text{NO}_2 \uparrow \]
Ti + 4 HF → TiF$_4$ + 2 H$_2$ ↑

TiF$_4$ + HNO$_3$ → TiF$_3$NO$_3$ + HF

TiF$_3$NO$_3$ + HNO$_3$ → TiF$_2$(NO$_3$)$_2$ + HF

TiF$_2$(NO$_3$)$_2$ + HNO$_3$ → TiF(NO$_3$)$_3$ + HF

TiF(NO$_3$)$_3$ + HNO$_3$ → Ti(NO$_3$)$_4$ + HF
Also, in the presence of nitric acid, the chem milling rate of the solution is reduced. Therefore, it is important to maintain a certain ratio of nitric acid to hydrofluoric acid (free acid) to achieve good chem milling results.
Considerations in Chem Milling

1. Type of alloys
   - Ti-6-4
   - Ti-Beta 21S

2. Forming methods

3. Geometry of parts

4. Parts racking/orientation

5. Parts movement
6. HF, HNO₃ and Ti concentration
7. Tank temperature
8. Tank mixing
9. Operator
Type of Alloys
Titanium 6Al-4V

• Typical alpha, alpha-beta Ti 6Al-4V, the following etchant performs well with etch rate about 0.8 mil/min.
• The free acid is between 2 - 5 N,
• Fluoride 3 – 8 N,
• Nitrate 0 - 3 N
• Dissolved Ti < 90 g/L
• 95 F
Titanium Beta 21S

• The following etchant works well with etch rate about 0.3 mil/min
• Free acid 6 - 14 N,
• Fluoride 2 – 7 N and
• Nitrate 4 - 9 N
• Dissolved Ti < 40 g/L
• 95 F
Forming Methods
SPF Titanium

- The following etchant gives good result with etch rate of 0.8 mil/min.
- Free acid 2 – 5.5 N
- Fluoride 3 – 8 N and
- Nitrate 0 – 3 N.
- Dissolved titanium < 90 g/L
- 95 F
Geometry of Parts
• Overall chem milling area
• Shape (sheet, cone, cylindrical, etc)
• Stock thickness
• Depth of cut
• Sides of etching (single, double)
• Complexity, 3-D structure
Racking/Orientation
• Sheet (vertical straight down, mid of tank depth wise).
• U-shape long blade, open end up and slanted.
• Cylindrical, small opening down when etches outside.
• Avoid gas trapping
• Past experience
Parts Movement
• Use only for intricate 3-dimensional etching
• 2 or 3 axis device.
• Rotation speed 0.5 – 1 rpm.
Titanium
Isogrid Duct
Chemical Concentration
• Relationship among free acid, fluoride, nitrate and dissolved Ti.
• Surfactant.
Tank Temperature
- Etch rate increases as temperatures increases.
- Etching process is an exothermal reaction that means heat will be generated during the process.
- Tank size
- Surface area to be etched
- Etching rate
- Agitation/mixing of the solution
- Depth of cut
Tank Mixing
• Homogenize temperature and acids
• Aeration
• Mechanical mixing
• Mixing frequency
• Mixing time
Operator
• Any procedures no matter how carefully designed and written serves no purpose if it is not prudently executed.

• Dedication
• Open minded
• Observance
• Accountable
• Integrity
• Always positive
SOLUTION CONTROL

- Free acid Titration
- Anions concentration determination
- Dissolved titanium concentration
- Surface tension
FREE ACID TITRATION

• INTERFERENCE FROM DISSOLVED METALS.
• REMOVAL OF INTERFERENCE
  – CHELATION
  – PRECIPITATION
• NaOH TITRATION TO END POINT
ANION CONCENTRATION

• FLUORIDE & NITRATE
• ANION CHROMATOGRAPHY
• INTERNAL STANDARD PREPARATION
TITANIUM CONCENTRATION

- TITANIUM – PEROXIDE COMPLEX
- SULFURIC ACID, PHOSPHORIC ACID AND HYDROGEN PEROXIDE ARE USED
- 395 nm MEASURING WAVELENGTH
SURFACE TENSION

- Measure with Surface Tensiometer at RT
- Typically kept below 40 dyn/cm
- Water surface tension at RT is 72.8 dyn/cm
IN CONCLUSION

CHEMICAL MILLING IS A POWERFUL AND VERSATILE METHOD IN SHAPING TITANIUM ALLOY PARTS WITH STRUCTURAL DETAILS.
IT IS AN ART!