Metal Finishing Workshop

Rochester Institute of Technology

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Acid Etching of Titanium Alloy Case Study

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Overview

• Introduce TECT Power Corporation
• Define Problem
• Understand the chemical reactions
  • Conduct research
  • Propose stoichiometric solution
  • Test proposed solution on bench scale
  • Confirm veracity of proposed solution
• Develop process alternative consistent with proposed stoichiometric solution
• Implement process alternative
• Measure results
Introduction to TECT Power Corp.

- Based in Utica, New York
- Manufactures turbine blades to stringent specifications
- Incurred large expenses in disposing of hazardous waste
  - Generated 502 tons of hazardous waste in 2007 from chemical etching operations
  - Spent $395K on purchase and disposal of etching acids
- Contacted local RTDC (MVATC) to find a P2 solution
- MVATC contacted NYSP2I, and a collaborative effort between TECT, MVATC, and NYSP2I was initiated
Define Problem

• Uses corrosive acids to mill blades to specifications
• Turbine blades are very expensive - $40K per blade
• TECT changes out acid baths frequently (once per week) so as to maintain reasonably constant acid etching rates; doesn’t want to overetch (and ruin) turbine blades
• TECT wanted to identify a means of reducing etching costs and waste, but did not replace process due to customer specification requirements
Understand Stoichiometry

Conduct Research

• Conduct literature search
• Determine chemical reactions of hydrofluoric acid (HF) and nitric acid (HNO$_3$) on titanium

Combine above reactions to obtain overall chemical reaction

$$\text{Ti} + 6\text{HF} + \text{HNO}_3 \rightarrow 2\text{H}^+ + \text{TiF}_6^{-2} + \frac{1}{2}\text{N}_2\text{O} + 2\frac{1}{2}\text{H}_2\text{O}$$

Note that molar ratio of HF to HNO$_3$ is 6:1!
Propose Solution

Next, determine composition of alloy by weight
- 90% titanium
- 6% aluminum
- 4% vanadium

Determine chemical reactions of hydrofluoric acid (HF) and nitric acid (HNO₃) on vanadium and aluminum

Combine above reactions using molar composition of alloy to obtain overall chemical reaction

\[
\text{Ti} + 0.12\text{Al} + 0.05\text{V} + 6.5\text{HF} + 1.1\text{HNO}_3 \rightarrow 2\text{H}^+ + \text{TiF}_6^{2-} + 0.12\text{AlF}_3 + 0.05\text{VF}_3 + 0.6\text{N}_2\text{O} + 2.8\text{H}_2\text{O}
\]

Note that molar ratio of HF to HNO₃ is still about 6:1!
Conduct Bench-Scale Testing

Test Conditions:
• 500 ml test volume in 1-liter beaker
• Initial acid concentrations at 9% HF and 12% HNO$_3$ as per customer specifications
• Etch titanium coupon for prescribed time period and boost to return acid concentrations to 9% and 12%
• Control temperature with ice bath at 80 deg F
• Run each etch cycle to nearly deplete HF
• Dissolved metal mass determined by weighing coupon on analytical balance
Confirm Veracity of Proposed Solution

The diagram shows the relationship between time in minutes and the amount of HF acid used, measured in mols. Three lines are plotted:

- **Beaker data**
- **Theoretical Ti only**
- **Theoretical - Ti alloy**

The x-axis represents time in minutes, ranging from 0 to 500. The y-axis represents the amount of HF acid used, ranging from 0 to 12 mols. The data points are scattered along the lines, indicating the progression of acid usage over time.
Application of Beaker Test Results

An understanding of the stoichiometry allows us to:

- Determine maximum waste generation
- Determine maximum total metal concentration
- Identify and avoid potentially unacceptable operating conditions
Determine Maximum Dissolved Metal Concentration

1. Titanium is added during etching
2. Dissolved titanium is removed with liquid to prepare for boosting

Mass Balance

Metal IN (etch) \[\rightarrow\] Metal OUT (boost preparation)

\[\text{At Steady State: Metal In = Metal Out}\]
Develop Mathematical Model

Mathematical Model Formulated to Simulate Beaker Test:

- Titanium dissolution – 6.5 moles HF per mole of Ti
- HF and HNO₃ acid concentrations initially set at 9% and 12%, respectively
- HF and HNO₃ acid concentrations are boosted at the end of each etch cycle to return to 9% and 12%, respectively
Model Predictions of Etch Process

Total Metal Dissolution

- Steady State ~130 g/l
Comparison of Model with Beaker Test Results

Math model and beaker data show good correlation.
Outcome of Steady State Evaluation

- Total metal concentration reached approximately 110 grams/liter at the end of the last beaker etch cycle.
- If the saturation concentration of dissolved titanium is greater than 130 grams/liter, then the etch bath could operate indefinitely without dumping (other than for maintenance needs), provided acid boosts were performed correctly.
- Operating in this mode reduces the quantity of hazardous waste generated to its minimum level because all tank dumping is eliminated.
Key Learnings from Lab Testing

• Proposed stoichiometric solution is correct
• No precipitation occurred up to 110 grams/liter of dissolved metal
• Etch rates remain constant over multiple boosts
• Multiple etch batches can be run without dumping when the acid boosts are properly conducted, so there is no need to dump acid baths so frequently!
Actual Results for 2009

• Proposed solution was partially implemented at TECT during the latter half of 2009
• Actual reductions in hazardous waste from chemical etching operations amounted to 292 tons per year in 2009 when compared to the baseline year of 2007
• This 58% reduction represents savings of $178,000 per year, and reflects both implemented P2 process improvements as well as decreased production.
Potential Results for 2010

- If TECT fully implements NYSP2I’s recommendations for all of 2010, hazardous waste from chemical etching operations can be potentially reduced by 431 tons (86%) if production volume returns to 2007 levels.
- This represents annual savings of $290,000 for the purchase and disposal of etching acids, due to the longer acid bath lives.
Questions and Discussion