Chemical Milling

Increasing Efficiency at Wyman Gordon Company

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Abstract

Chemical Milling is a finishing process that removes oxide scale and alpha-case from forged titanium parts. To increase the efficiency of chemical milling at Wyman-Gordon Company, we analyzed previous projects, assessed the etch quality of their chemical milling bath, and evaluated means of process control and potential areas of cost and raw material savings. Via our experimentation we determined that the ideal concentration of HF is 8% for all temperatures 90°F-120°F to effectively etch a titanium part.

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Executive Summary

The purpose of this project was to determine ways to reduce costs associated with the chemical milling process utilized to remove oxide scale and alpha-case from titanium alloy forgings at the Grafton, MA facility of Wyman-Gordon Company. Our principle methods of research involved the evaluation of previous project research and Wyman-Gordon procedural documentation, and then the scale down of the chemical milling process to allow for laboratory experimentation.

This experimentation investigated the effect of Temperature, Hydrofluoric acid concentration, and titanium concentration on the etch rate of the acid bath on Ti-6Al-4Va test pieces. The variable parameters were determined via Wyman-Gordon operating specifications and were as follows: temperatures of 90° F, 105°, and 120°, hydrofluoric acid volume percents of 7%, 8%, and 9%, and Titanium concentrations of 0 g/l, 10 g/l, and 20g/l.

Analysis of the data provided valuable insight into the chemical milling process. The most useful observation of the many correlations observed was that the acid etch rate remained relatively stable with respect to other variables at the medium [HF] level of 8% vol. Although they are not fully conclusive, additional observations from the data represent an initial guide to further experimentation.

From our research we discovered several avenues for improvement for Wyman-Gordon’s chemical milling process. These included developing a greater understanding of the process so that an effective automated control scheme could be implemented, optimizing the process by collecting data and implementing procedural changes based on the results, preventing excessive waste by developing means to prevent mid-process waste and reclaim end-process waste. Additionally, experimental research into the feasibility of using fluoroboric acid instead of hydrofluoric acid may lead to both chemical and economic benefits.

We conclude that by implementing our recommendations, Wyman-Gordon Company will be able realize cost savings and quality improvement in the short and long term.

1. Introduction

In the current economic climate, companies across the world are looking to increase efficiency of their operations. Wyman Gordon Company (WG) is dedicated to the production of high quality parts with applications in the medical, aerospace, and power generation industries. At their Grafton, Massachusetts facility, WG produces the majority of their aerospace parts for companies such as Boeing, Lockheed Martin, and Sikorsky. All parts must conform to standards set by each of these companies to insure acceptable performance levels.

The process of concern at WG is the chemical milling process. This process is used to remove undesirable qualities formed as a product of forging. By removing these qualities, all parts achieve the specifications of the consumer. The chemical milling process is one that incorporates hydrofluoric and nitric acids, which are two hazardous and expensive acids. The objective of this group is to increase efficiency of the process by optimizing the lifetime of each acid bath and recommending acid bath alternatives to WG.

2. Background

Improvements to the current chemical milling process at WG should be made with a developed understanding of titanium, titanium processing, and its interactions with other species. In this section, we provide a brief history of titanium and how it was discovered. Next, we delve into the concept of alpha case formation and the kinetics involved. Following alpha case, we explain the current production process of WG to outline the steps required to make a part. We then focus on the chemical milling step by giving a history of the process and describing some of the acids used therein. Finally, we discuss previous MQP's at WG and how they pertain to this project.

2.1 Titanium

Titanium is the 22nd element in the periodic table with the symbol Ti. It is used in many applications due to its high strength to weight ratio. "In 1791, William Gregor, a clergyman and mineralogist, discovered a black magnetic sand oxide of an unknown element from the parish of Menaccan in Cornwall, England. He then published an account of his investigations and called the new element menaccanite. Meanwhile, a German chemist by the name of M.H. Klaproth was investigating a mineral known as rutile. After rigorous examination of the oxide, Klaproth came to call this new element titanium for the Titans of mythology. Additionally, he found a sample of ilmenite that also contained titanium, which was identical to Gregor's menaccanite (McQuillan, 1956, p.1)."

2.2 Ti-6Al-4V

"The simplest α+β alloy is Ti-6Al-4V. α+β alloys typically exhibit good fabricability, high room temperature strength, and moderate strength at higher temperatures. Additionally, such alloys may contain between 10% and 50% β, otherwise they are not weldable (McQuillan, 1956 p.2)."

2.3 Alpha Case

Alpha case is an outer layer that forms on a Ti alloy part after it is heat treated. Due to exposure to oxygen, the outer layer tends to have greater alpha character rather than the desired alpha + beta. The alpha case that forms decreases the strength of the part and increases the hardness, causing parts to fail under higher stresses. If a part is exposed to high stress on the surface, a fracture may occur within the alpha layer and continue to propagate through the alpha + beta layer regardless of the higher stress tolerances within the inner layer. By removing alpha case, alpha + beta character is maintained and the titanium part can tolerate higher stresses and meet specification.

2.3a Alpha-Case Formation Kinetics

Chemical Milling by Harris (1976 p404-405), gave insight into the kinetics of alpha-case formation. In 1950, W.A. Alexander and L. M. Pigeon investigated the relationships between oxygen and titanium. More specifically, they analyzed the rate at which oxygen reacts with titanium powder and sintered bar. In their experiments, they applied heat for 20 hours and operated at temperatures ranging from 20 to 550°C in an oxygen rich atmosphere at 20 mm of mercury. From their results they concluded that the oxygen-titanium interaction could be modeled by Equation 1:

$$\ln(t+3) = k_1V + k_2 \qquad (1)$$

t is measured in minutes, V represents the total volume of oxygen absorbed and k_1 and k_2 are constants that vary with reaction temperature. Additionally, it was found that oxygen pressure increased to 30 mm of mercury at 156°C, thus causing a decrease in the absorption rate of oxygen. This was later confirmed by J.T. Waber, G.E. Sturdy, and E.N. Wise by using spectrophotometric techniques to measure the thickness of tarnish on the surface of the titanium against time via changes in reflectivity. The resulting expression for the growth of an oxide film is Equation 2:

$$\lambda = kln(t+1) \qquad (2)$$

λ is the thickness of the oxide film, t represents time, and k is a constant with temperature dependence. This expression was supported by N. Cabrera and N.F. Mott who studied the oxidation of a metal surface at temperatures lower than that necessary for normal thermal diffusion and hypothesized a logarithmic rate law. They also conducted experiments at high temperatures, where small-finite films are produced and then replaced by scaling reactions causing continuous film growth. Furthermore, oxygen begins to dissolve in the metal lattice at higher temperatures. Addressing this issue, Alexander Pigeon found that from 350°C-550°C the isothermal oxygen absorption/time curves were asymptotic to the curve represented by Equation 3:

$$\ln\frac{(c-c_f)}{(c_i-c_f)} = -k - t/\tau \qquad (3)$$

Where c is the amount of oxygen absorbed in time t, c_f is the final concentration of oxygen in the metal (assumed to be equivalent to the oxygen concentration of TiO_2), c_i is the initial concentration of oxygen represented as impurity metal, τ is a constant dependent on the rate of diffusion of oxygen in the metal lattice at the temperature under consideration and k is a constant that also has temperature dependence. From this relationship, the oxidation rate of the metal just above 350°C is controlled, after initial deviation via diffusion. However, E.A. Gulbransen and K.F. Andrew found that the oxidation rate law from 350°C-600°C was parabolic. Operating under 76 mm of mercury and using a microbalance technique for determining oxygen absorbance, Gulbransen and Andrew expressed their results as Equation 4:

$$w^2 = k_1 t + k_2 \qquad (4)$$

2.4 Wyman Gordon Production Process

The following stages of production are necessary to provide the consumer with their desired part. Not only are the sections sorted by operation, they are also physically sorted throughout the plant so that the part may enter one end of the facility and travel through a near assembly line style of production. Each section is provided to develop one’s knowledge of the entire process.

2.4a Order Entry and Planning

WG's IQP division receives contact from the consumer and records the desired specifications of the part(s). They also handle the scheduling for delivery.

2.4b Material Procurement

WG's COP division ensures that the required raw materials for production are available. Materials are typically in billet form, raw material that has not undergone machining. Products include: Titanium, Nickel-Based, Steel, Powder, and Aluminum Alloy.

2.4c Stock Cutting

WG's SC-G and WG-WSTK remove any unnecessary material from the billet to ease the process of forging.

2.4d Forging

WG's FS, ISO, and/or ISO-ERIE groups manage the forging operations. These operations include: open die forging, and closed-die forging. According to (Cayer, et al. 1997), "open dies are used for pre-shaping operations such as elongating, flattening, and/or widening of the pieces. Close-die forging is used to assume the near final dimensions of the part."

2.4e Machining

WG's MS-1, ang WMS groups deal with machining of parts. Machining is necessary to remove any access material left over from forging and brings the part closer to its final dimensions. According to (Cayer, et al. 1997), the machining processes in use are: hot trimming, sawing, flame, and cutting.

2.4f Inspection

WG's PROC-CON, WIPC, and PROC-CERT groups conduct non-destructive testing on the test pieces to determine any imperfections in the part. Testing includes: ultrasound and microscopy.

2.4g Heat Treatment

WG's HTS and WHTS groups handle all annealing operations. These operations are necessary because parts are exposed to high strains via forging and annealing removes them.

2.4h Testing

WG's FDI-1, PROC CERT, TEST, and WIPC groups are responsible for testing. Once the part leaves heat treatment it has to be inspected. If it passes inspection, it moves on to the chemical milling or oxide scale removal process depending on if the part is Ti or Ni based respectively. If the part shows no imperfections after chemical milling/oxide scale removal it proceeds to additional testing for failure in the piece.

2.4i Certification

WG's CERT-REL group manages the certification of the product. They complete the final inspection of the part to see if all specifications are met and pass or fail the part to be shipped.

2.4j Packing & Shipping

WG's PKG and WPI groups prepare the orders for shipment. Parts proceed via truck for further transportation via truck, boat, or aircraft.

2.6 Acids of Interest

2.6.1 Hydrofluoric Acid

Solution of hydrofluoric acid in concentrations ranging from 10 percent to full strength will descale superficially oxidized titanium by dissolving the metal underlying the scale, but the scale itself must first be broken to allow contact between the acid and the metal. A simple descaling process of this type has the advantage that it involves very low equipment and operating costs, but the loss of metal is high. Final surface cleaning after descaling by other methods may be achieved by a short dip (10-60 seconds) in a concentrated hydrofluoric acid solution (1 p.97).

2.6.2 HNO_3 & HF mixtures

“Mixtures of nitric and hydrofluoric acids widely varying compositions are used both for descaling and for surface brightening. Descaling may be carried out at about 60° C in a bath containing 8 percent nitric acid and 2 percent hydrofluoric acid. The action is similar to that of hydrofluoric alone, i.e. the removal of scale by attack of the underlying metal, and the scale must be broken in order to allow the process to occur. Treatments in more concentrated nitric acid-hydrofluoric acid solutions lasting only a minute or two are used after mechanical or fused salt descaling processes for surface brightening. Recommended compositions include three parts nitric acid-one part hydrofluoric acid, ten parts nitric acid acid-two parts hydrofluoric acid, and ten parts nitric acid-two parts hydrofluoric acid-five parts water. Bath temperatures are in the range 60-70° C. The danger of hydrogen contamination occurring during pickling is reduced if the nitric acid content of the pickling solution is increased (1 p.98).”

2.6.3 HBF_4

“Surface scales formed on titanium are penetrated by fluoroboric acid, and subsequent dissolution of the underlying metal causes the scale to flake off. The surface is attacked uniformly, and no embrittlement occurs, but a considerable amount of metal is lost. Solutions containing 5 percent or more of fluoroboric acid are used at about 90° C, and the treatment times required are of the order of 10 minutes (1 p.98).”

2.7 Previous MQP’s

2.7.1 Pollution Prevention at the Wyman Gordon Company (1994)

In 1994, N. Burnham and F. Dannheim et. al. completed a project in conjunction with Wyman-Gordon Company in Grafton, MA analyzing the chemical milling process employed at the plant. Below is the abstract for the report:

> Abstract: The chemical milling process, on the Wyman-Gordon Company's sources of waste acid, is analyzed and methods are determined to minimize the by-products of titanium etching in the K-1 tank. Studies were performed to determine optimum etching times for titanium parts, methods of acid recovery, and measure to minimize evaporative losses. Vacuum distillation and diffusion dialysis systems are examined for their acid recovery potential and economic feasibility.

In 1993, the company used approximately 36,000 gallons of HF and HNO_3. The report noted that there were three principle ways in which acid from the K-tank was wasted: evaporation, carry over losses to the K-2 rinse tank, and disposal of entire tank contents upon reaching the specified tank Ti capacity (30-59 g Ti/ l of solution). The amount of total disposed spent acid waste was 165,000 gallons. In 1993 dollars, this waste represented approximately $152,000 worth of liquid acid.

The report proposed a number of possible strategies to recover the waste acid from the process:

> "Possible recovery solutions are: process changes, optimizing the amount of metal removed from each forging; acid recovery systems, which would allow for the recovery and reuse of the spent acid, thereby reducing both the raw chemical costs and waste disposal costs; the final option is the improvement of operating methods which would reduce the amount of acid lost by evaporation and carry over."

As the aim of the report was pollution prevention, the report contains a significant amount of background material on the history of environmental government involvement as well as the current standards and practices of governmental agencies like the EPA. Of particular note is the EPA's hierarchy of ways to minimize hazardous waste. The hierarchy shown in Figure 3 ranges from most to least desirable method for hazardous waste minimization.

Furthermore, it is noted in the report that waste minimization has numerous positive outcomes that would be in the company's best interest to achieve, regardless of regulations. These outcomes are itemized in Figure 1, below.

- Reduce compliance costs for permits, monitoring, and insurance
- Lower risk of spills, accidents and emergencies
- Lower long term environmental liability and insurance costs
- Reduced pollution costs through better management and efficiency
- Income derived through sale or reuse of waste
- Reduced effluent costs and assessments from local wastewater plants

Figure 1: Positive Outcomes of Waste Minimization

The project methodology can be reduced to the steps shown in Figure 2.

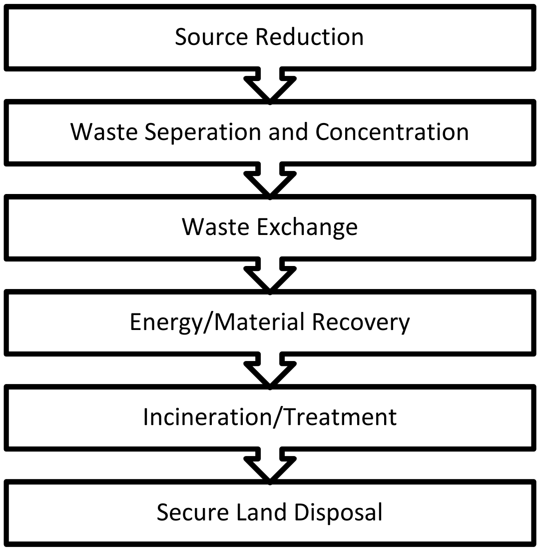

Figure 3: EPA Hierarchy for Waste Minimization

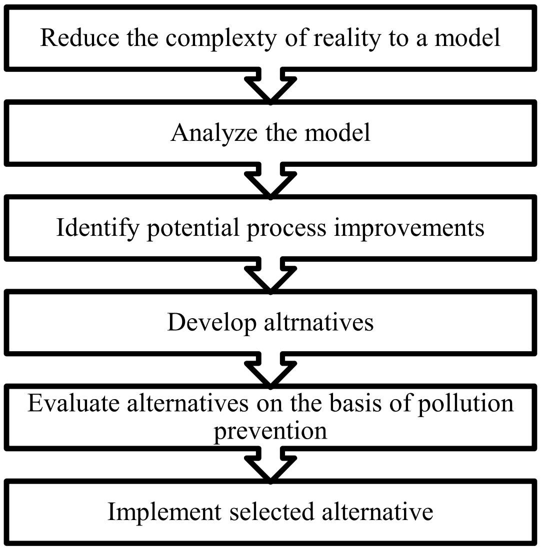

Figure 2: Project Methodology

Mass Balance Analysis

The tank was filled approximately once every two weeks. The mass balance itself was carried out by inspecting plumbing department and Lab records. 14% of the losses from the K-1 acid tank result from evaporation. Through experimentation the group found that the best way to prevent this kind of loss was through use of a floating media such as balls, discs, or cones.

Process optimization

The group conducted heat treatment experiments to try to reduce the development of alpha-case and an oxidized layer on the titanium.

Further recommendations

The change from the .02 in removal standard to the .015 removal standard must be executed by workers on the floor. In 1993, full implementation of the .015 in removal standard saved the company $13,300 annually.

Conclusion

Two different types of acid reclaimers were examined: an “Acid Recycling System” produced by Pure Cycle Environmental Technologies, and a “Waste Acid Detoxification and Recovery System” developed by Pacific Northwest Laboratory. These systems had the potential to save up to 95% of the 1993 acid purchases.

Results

The group performed a “life cycle” study for the chemical milling process over its normal cycle, two weeks. The breakdown for where Acid Waste leaves the tank is as follows: 80.9% was removed at the end of the two weeks and dumped; 14.2% was lost via evaporation; 4.9% was lost via drag out into the K-2 water rinse tank. These numbers do not include the acid consumed in the removal of titanium Alpha Case from the forgings. The percents are essentially “volume losses.”

Minimization of evaporative losses

The group conducted experiments to determine what kind of floating media would most effectively mitigate evaporative losses. They ultimately found weighted balls to be the most effective, causing a 49.3 % reduction in evaporative losses.

Acid recycling systems

The system that was analyzed for recyclization of acid was the Pure Acid Recycling system. A full economic analysis was prepared and the system was found to create an annual savings of $232,551.

2.7.2 Alpha Case Formation and Forge Lubricant Analysis (1997)

In 1997, Jeffrey Cayer and Jebediah Ledell et. al. completed a project in conjunction with Wyman Gordon Company (W.G.) in Grafton, MA evaluating the formation of alpha-case on Titanium alloy parts and ways to inhibit its formation during forge productions. The alloy used to simulate alpha-case formation was $TiAl_6V_4$. Prior to forging, W.G. places an SJ coat on each part to prevent interaction by outside molecules. Interaction by outside molecules, changes the properties of the titanium work piece and causing it to fail the standards set by the consumer. This group tested the amount of alpha-case build-up on titanium parts that were not coated with SJ, coated, and forged in a controlled oxygen environment.

There were three major pieces of equipment used to test the level of alpha-case build up on the titanium pieces: an electric furnace, forge press, and an abrasive saw. To heat pieces to 1750 °F and anneal at 1300 °F, a General Sigma's Lindberg electric furnace at W.G.'s Research & Development facility in Millbury, MA was used. The forging press used was a 1500 ton, hydraulic forging press also located within W.G.'s Research & Development facility in Millbury, MA. The die on the forge press kept a temperature of 800 °F and operated at a velocity of 5 inches per minute. The press forged 2.5x 1.5x 1.5 titanium samples that were cut using a Struer's abrasive saw. To simulate a low/controlled oxygen atmosphere, a stainless steel rectangular encasement was inserted into the furnace and fed with compressed gas. The level of oxygen was regulated at 1.0ppm and 8000ppm with argon gas. All non-coated, and coated sample were pre-heated, forged, and the annealed. All controlled atmosphere samples were pre-heated and annealed under low/controlled oxygen level conditions. The group observed that the non-coated titanium samples developed 95% of the alpha-case in the pre-heat and first forging steps. It was also observed that a sample exhibited a loss of alpha-case in the annealing phase. If this sample is excluded, 70% of alpha-case to developed in the pre-heat and first forging steps. For the SJ coated samples, alpha-case levels were lower than non-coated samples. It was found that the majority of alpha-case developed during the first forge and one sample developed alpha-case during the pre-heating step. The low alpha-case levels were attributed to the formation of Al_2O_3, which acted as a barrier due to its properties of stability and high melting point. Additionally, when pieces were handled pieces of the coating began to flake off, thus weakening the barrier to alpha-case formation. Also, during the forging steps, the dies caused an uneven layer of SJ coating, weakening the barrier to alpha-case formation. This was confirmed by the increased of alpha-case formation in the annealing step. One sample was coated with 2.5 times the level of SJ coating than the others. It demonstrated a higher tolerance for alpha-case formation, exhibiting lower levels than the other samples. For the conditions of low/controlled oxygen levels, samples exhibited lower levels of alpha-case than both the non-coated and coated samples. However, for 1 ppm and 8000 ppm oxygen conditions, the titanium samples exhibited similar levels of alpha-case. In addition, the level of alpha-case found between the second forging and annealing steps, both coated and controlled atmosphere samples had similar levels of alpha-case.

This group had a large focus on finding ways to lower levels of alpha-case. The SJ coated samples proved to be a barrier to alpha-case conversion and could be reapplied to the titanium piece to maintain that barrier. The controlled/low oxygen environment was impractical in a manufacturing setting, increasing costs of production via installation and maintenance. It was recommended that W.G. take several steps to improve the prevention of alpha-case formation. Viewing alpha-case by hardness testing and a color ratio analysis of the microstructures would prove more precise than the method by thermal print and ruler. Additionally, weighing samples before and after coating would allow for a better estimate of SJ coating thickness. Moreover, weighing before and after annealing, would allow for a measurement of alpha-case increase or decrease. Lastly, titanium samples run in duplicate would create more data points, thus creating repeatability and lowering sources of error.

2.7.3 An Analysis of Etch Tanks at Wyman Gordon Company (1998)

In 1998, Harting et. al., studied the chemical milling process at Wyman Gordon to evaluate its efficiency and to see if there were alternative procedures for milling titanium. The group scaled down the current bath to test the effects of temperature, agitation, titanium concentration, and hydrofluoric acid concentration on etch rate. Additionally, they tested the etch rates of copper sulfate pentahydrate, and fluoroboric acid in comparison to hydrofluoric.

Agitation is necessary because it allows for a uniform concentration of each species throughout the bath. The group ran experiments at no agitation, low agitation, medium agitation, and high agitation. They found that medium agitation resulted in the best etch rate under safe conditions.

When temperature was tested, the effect on the etch rate was steadily increasing from 110°F to 140°F, where it began to level off. This shows that etch rate increases with temperature up to 140°F.

Hydrofluoric acid was tested at 8%, 6%, 4%, and 2% of the simulated bath. As the concentration of HF decreased, so did the etch rate. This showed that 8% of hydrofluoric acid is necessary for higher etch rates. Additionally, the group noted that the etch rate began to plateau after 8% hydrofluoric acid, demonstrating an approximate maximum etch rate at 12% HF.

Testing for titanium concentration was very inconsistent. In order to see a trend in etch rate vs. titanium concentration one must isolate all other variables. In this case, the concentration of hydrofluoric acid ranged from 4.5% to 8%. The group found that the etch rate of titanium increased with lower concentrations of titanium, but their data showed instances when higher concentrations of titanium gave higher etch rates than lower concentrations of titanium. Concentrations of hydrofluoric would have provided a more thorough understanding of the relationship not only between titanium and etch rate, but titanium concentration and hydrofluoric acid concentration, if reported for each run. Increased HF content alongside increased Ti content could yield higher etch rates than constant HF and low Ti content.

Copper sulfate pentahydrate and fluoroboric acid were tested to determine an average etch rate. In comparison to hydrofluoric acid, copper sulfate pentahydrate achieved approximately one third of the etch rate and fluoroboric acid achieved 80% of the etch rate. The group suggested that fluoroboric acid may be a viable candidate for replacement of hydrofluoric acid.

3. Methodology

3.1 Scope of Project

The goals of this project are twofold: to develop cost savings methods for the chemical milling process utilized by the Wyman-Gordon company to remove the layer of oxide scale and alpha case from titanium alloy forging; and to assist in assessing the etch quality in a related chemical process utilized to expose {What kind of imperfections} imperfections on the surface of nickel alloy forgings. These goals were developed through conversations with Wyman-Gordon principals, observation of the current process, background literature research, examination of Wyman-Gordon procedural documents, and a general knowledge of chemical engineering design principles.

3.2 Methods of cost savings for the K-Tank Chemical Milling Process

In order to develop cost savings methods for the chemical milling process first the group had to determine what areas of the process could be improved. A thorough inspection of the chemical milling process led to the development of four questions of importance in attempting to find ways for Wyman-Gordon to reduce the cost of the chemical milling process in the general scheme of production. These questions encompass each of four distinct life periods of the acid process, namely preparation of the bath, maintenance of the bath, use of the bath, and replacement of the bath and are as follows:

- *Is there a more economical acid solution to use in the chemical milling process?*
- *If the current acid solution is the best, or most viable, what operating conditions are "best;" what operating conditions are "acceptable?"*
- *When a forging is actually dipped into the solution and chemically milled, are there procedural and/or equipment changes that can be made to improve the efficiency with which the process utilizes milling potential (via the solution "moving" toward equilibrium) to remove material from the forging?*
- *What is the true cost of replacing the "spent" acid bath with a virgin acid solution?*

3.2.1 Appropriate Operating Conditions

Until such time as there is a change in the make-up of the acid bath, optimizing the current process to utilize the chemical milling capacity of the bath to its fullest is of great importance to realize cost savings. In order to make any propositions to changes to the current Wyman-Gordon procedures, first our group had to develop an "operating profile" describing the operating conditions under which the bath "works." Then, by using this information in comparison with documentation on the current "bath lifetime" history we could potentially find deviations from the two that would lead to cost savings.

3.2.2Variables

The main independent variables of interest in the process were the Titanium concentration of the bath, the hydrofluoric acid of the bath, and the temperature. The dependant variable of interest was the rate at which the bath removes material from the surface of the forging, denoted as the etch rate. The nitric acid concentration was also an independent variable but it was demonstrated in *The Physical Metallurgy of Titanium Alloys,* that nitric Acid had little effect on the Etch rate.

3.2.2.1 [Ti]

It is known by those who operated the chemically milling bath that the greater the quantity of Titanium there is in the bath, the slower the etch rate. At a certain point the solution reaches equilibrium and fails to etch a part any more. Due to production considerations, the bath was often changed before it actually reaches this point of no etch. If a more comprehensive knowledge of the [Ti] dependence of the Etch rate was achieved it could lead to economically beneficial procedural changes to fully take advantage of a single bath preparation.

3.2.2.2 [HF]

The main milling agent in the bath is hydrofluoric acid. The current specification for the operating range of the bath with respect to the concentration of hydrofluoric acid is seven volume percent, plus or minus 1 percentage point. When the bath falls below this range it must be spiked with additional acid, sometimes necessitating decanting the bath to facilitate the added volume of the acid spike, to bring it back within the operating envelope. A more comprehensive understanding of the envelope of operating of the bath with respect to [HF] would allow the development of an optimum decanting/spiking procedure. This optimization would be beneficial for both cost and production speed considerations.

3.2.2.3 Temperature

There is an operating temperature envelope that has its minimum set by the required temperature to mill a part and its maximum set to minimize the deleterious effects of hydrogen embrittlement. The reaction that takes place when a part is chemically milled is exothermic. Thus, the bath temperature increases during the milling procedure. The procedure for tank operation therefore must address both the maintenance of the tank at an operational sounds minimum temperature, and the prevention of exceeding the maximum. With a greater understanding of the temperature dependence of the etch rate the operational envelope could be extended to include lower minimum temperatures. This could have a deleterious effect on production speed but a beneficial effect on cost.

3.2.3 Economic Benefit of WG operating and servicing procedure change

In each of the above cases a greater understanding of the operating envelope of the bath could lead to a change in the actual operating conditions of the bath, leading to cost savings. An economic analysis of the effect of each of the possible changes with respect to the different variables will allow for a true comparison.

Knowledge of the titanium concentration dependence of the Etch Rate could lead to increased etch capacity of a single bath preparation. Thus cost savings would present themselves as decreased acid cost. In addition, a procedural change that would forbid the spiking of a bath near the end of its titanium concentration life-cycle would prevent the waste of acid, further decreasing the cost of the process.

Knowledge of the hydrofluoric concentration dependence of the etch rate, leading to an optimized decanting/spiking procedure would be multifold in its benefits. It would decrease waste of acid, it could lead to increased production speed by maintaining the optimal (maximum) etch rate. Furthermore, to a certain extent, it would help maintain the tank at a constant etch rate – this would benefit the quality aspect of chemical milling, that is, the consistency of the etch attained based upon the part specific procedure.

Knowledge of the temperature dependence of the etch rate, leading to an optimal temperature maintenance procedure for the bath, could lead to cost savings. If the bath could be kept at a cooler temperature it would a) decrease the heat duty of the heat exchanger, and b) decrease the amount of acid solution lost by evaporation.

3.3 Experimental Methods

3.2.1 Equipment

The hydrofluoric experiments required a wide variety of instruments to retrieve data. For these experiments, a 1000 ml plastic beaker was needed to host the acid bath. That beaker sat within a 2000ml glass beaker with 500 ml of water and a magnetic stirrer. Temperature was monitored with a 14 inch glass thermometer. A plastic air hose agitated the acid bath during experimentation. To hold the 12 1”x1”x.5” Ti-6-4 samples, a sample was tied to a 10 inch piece of insulated wire and suspended via a vertical stand in the acid bath. For heating of the bath, a hot plate equipped with stirring capabilities was utilized. Cooling of the bath took place in a 2 gallon plastic tray filled with ice cubes. Rinsing of the test pieces was carried out with a 600 ml glass beaker filled with 400ml of water. The timing of the spiking and testing cycles was accomplished via a wrist watch with a built in timer. Ten milliliter samples of the acid bath were taken via a suctioning pipet and placed in a 100 ml plastic beaker. The titanium concentrations were determined via an atomic absorption machine (list specific model). A titration was utilized by a lab technician to determine hydrofluoric and nitric acid concentrations

The specific pieces of equipment that were utilized in the experimentation are listed below:

- 1000 milliliter plastic graduated beaker with top side flaps
- 2000 milliliter glass graduated beaker
- 600 milliliter glass graduated beaker

- 3x100 milliliter plastic beakers with stoppers
- Magnetic stirrer
- 14 inch glass thermometer
- 3 foot plastic hose
- Laboratory hood equipped with air valve
- 12, 2”x 1”x 1” Ti-6-4 test pieces
- 4 feet of insulated wire
- 1 hot plate with stirring capabilities
- 2 gallon plastic tray
- 1 stop watch
- 1 graduated pipet with one-way valve
- 1 graduated pipet with suction for sampling
- 1 vertical stand, with clamps
- 5 liters of 50% hydrofluoric acid
- 5 liters of 50-70% nitric acid
- .25 liters of acetone

The following pictures depict the components of our experimental testing procedure. Figure 4 displays the test pieces utilized in the experiment. Figure 5 shows the equipment setup for all trials of the scaled down acid bath. Figure 6 illustrates the scaled down acid bath during the processing of a titanium test piece.

Figure 4: Ti-6Al-4Va 2" x 1" x 1" test samples

Figure 5: Laboratory setup for scaled down hydrofluoric acid bath

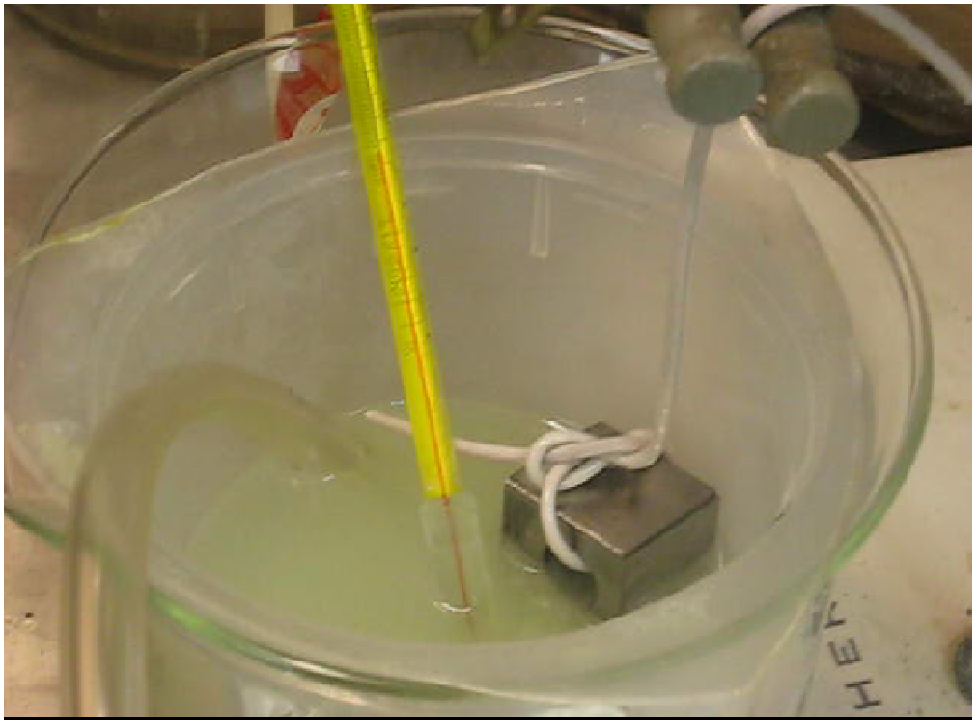

Figure 6: Overhead view of laboratory setup during a test trial

3.2.2 Procedure

Procedure for 7% HF Experiments

1. Add 249 ml of HNO_3 to 2000ml beaker to achieve 83% by volume
2. Add 30 ml of HF to 2000ml beaker to achieve 7% by volume
3. Add 21 ml of H_2O to 2000 ml beaker to achieve 10% by volume
4. Add 400 ml of H_2O to 600 ml beaker
5. Utilize Bath Change Procedure

Procedure for 8% HF Experiments

1. Add 246 ml of H_2O to 2000ml beaker to achieve 82% by volume
2. Add 24 ml of HF to 2000ml beaker to achieve 8% by volume
3. Add 30 ml of HNO_3 to 2000 ml beaker to achieve 10% by volume
4. Add 400 ml of H_2O to 600 ml beaker
5. Utilize Bath Change Procedure

Procedure for 9% HF Experiments

1. Add 243 ml of H_2O to 2000ml beaker to achieve 81% by volume
2. Add 27 ml of HF to 2000ml beaker to achieve 9% by volume
3. Add 30 ml of HNO_3 to 2000 ml beaker to achieve 10% by volume
4. Add 400 ml of H_2O to 600 ml beaker
5. Utilize Bath Change Procedure

Bath Change Procedure (7% HF, 8%HF, 9%HF)

0 grams of Titanium, 90°F

1. Using virgin bath, agitate and heat acid bath to 90°F
2. Follow Generic Test Piece Procedure

0 grams of Titanium, 105°F

3. Increase temperature to 105 °F and agitate
4. Follow Generic Test Piece Procedure

0 grams of Titanium, 120°F

5. Increase temperature to 120 °F and agitate
6. Follow Generic Test Piece Procedure

10 grams of Titanium, 90°F

7. Agitate and bring acid bath to 90°F
8. Follow Bath Spike Procedure
9. Follow Generic Test Piece Procedure

10 grams of Titanium, 105°F

10. Increase temperature to 105 °F and agitate
11. Follow Bath Spike Procedure
12. Follow Generic Test Piece Procedure

10 grams of Titanium, 120°F

13. Increase temperature to 120 °F and agitate
14. Follow Bath Spike Procedure
15. Follow Generic Test Piece Procedure

20 grams of Titanium, 90°F

1. Agitate and bring acid bath to 90°F
2. Follow Bath Spike Procedure
3. Follow Generic Test Piece Procedure

20 grams of Titanium, 105°F

4. Agitate and bring bath to 105 °F
5. Follow Bath Spike Procedure
6. Follow Generic Test Piece Procedure

20 grams of Titanium, 120°F

7. Agitate and bring bath to 120°F
8. Follow Bath Spike Procedure
9. Follow Generic Test Piece Procedure

Generic Test Piece Procedure

1. Collect sample for titration to determine HF and HNO_3 concentrations
2. Collect sample for atomic absorption to determine Ti concentration
3. Clean test pieces with acetone
4. Run test piece for 2 minutes in acid bath
5. Rinse test piece in water bath
6. Measure inches removed from test piece
7. Run test piece for 10 minutes

8. Rinse test piece in water bath
9. Measure inches removed from test piece

Bath Spike Procedure

1. Run spike piece until desired Ti concentration achieved
2. Run atomic absorption to determine concentration of Ti
3. When desired concentration is achieved, run titration of HF and HNO_3
4. Balance HF, HNO_3, and H_2O based on volume of bath and concentrations
5. Bring bath back to desired temperature

3.2.1.3 Data Collections

The data that will be collected is the same for each trial. The times of 2 and 10 mins will be recorded for the time the test piece is run. The starting temperature for the solution as well as the temperatures after the 2 minute and 10 minute runs will also be recorded. The initial thickness of the test piece as well as the thickness after the 2 minute and 10 minute runs will be recorded to determine the etch rate of the bath.

4. Results & Analysis

This section highlights the findings from the hydrofluoric bath experimentation.

4.1 Hydrofluoric Bath Results

The results from each of the tested variables are necessary to improve upon WG's chemical milling operations. With a comprehensive model of these variables, WG may use this data to implement a more effective control scheme for the process.

The following were the most important observed trends from the experimental data.

i. At low [Ti], etch rate suffers with higher temperatures.
ii. At high [Ti], etch rate benefits from higher HF and increasing temperature.
iii. At high HF, etch rate suffers with higher titanium concentrations at low temperature.
iv. At low temperatures, etch rate suffers with high titanium.
v. At high temperatures, etch rate suffers in low acid.
vi. At low HF, etch rates are relatively lower.
vii. At medium HF, etch rate is relatively stable with respect to other variables.

4.1.i Low Titanium

The following figure is a plot of etch rate against Temperature for the case of low titanium. The figure clearly shows that the etch rate decreases with increasing temperatures at low [Ti]. For example, in the case of a 9% HF solution, the etch rate falls from .0339 mm/min to .0264 mm/min over a 30 °F temperature change.

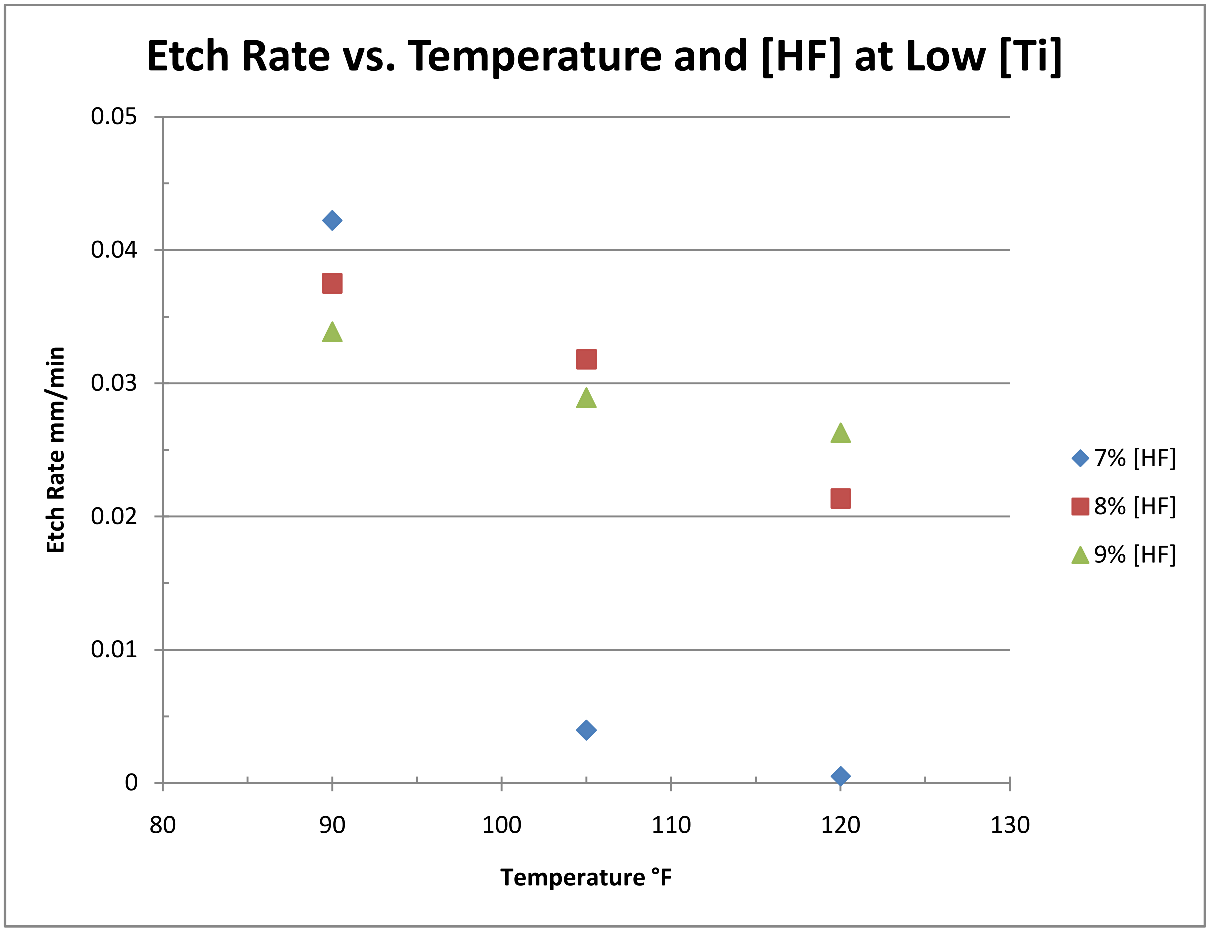

Figure 7: Etch Rate vs. Temperature and [HF] at Low [Ti]

4.1.ii High [Ti]

The following figure is a plot of etch rate against Temperature for the case of high titanium. The figure clearly shows that the etch rate benefits from increasing [HF] and temperature at high [Ti]. For example at 90°F the etch rate for 7% HF is nearly 5 times lower than the etch rate for 8% HF. This diversion decreases with increasing temperature. In addition, for 8%HF, the etch increases from .0328 to 0.347 over a 30°F temperature change.

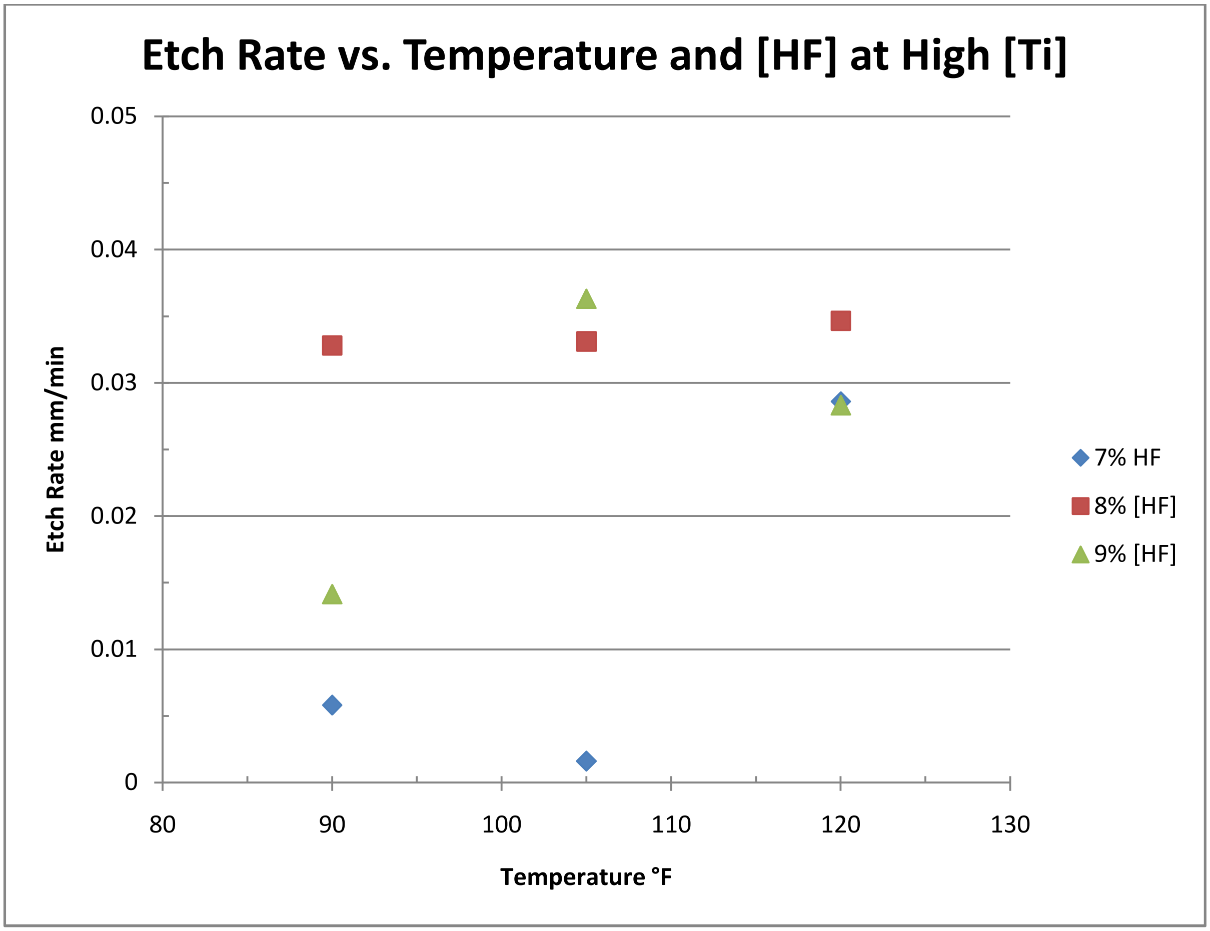

Figure 8: Etch Rate vs. Temperature and [HF] at High [Ti]

4.1.iii High [HF]

The following figure is a plot of etch rate against [Ti] for the case of high [HF]. The figure clearly shows that the etch decreases with an increased titanium concentration for the case of low temperature. For example, in the case of a 90° F solution, the etch rate falls from .0339 mm/min to .0142 mm/min over a 20 g/l change in [Ti].

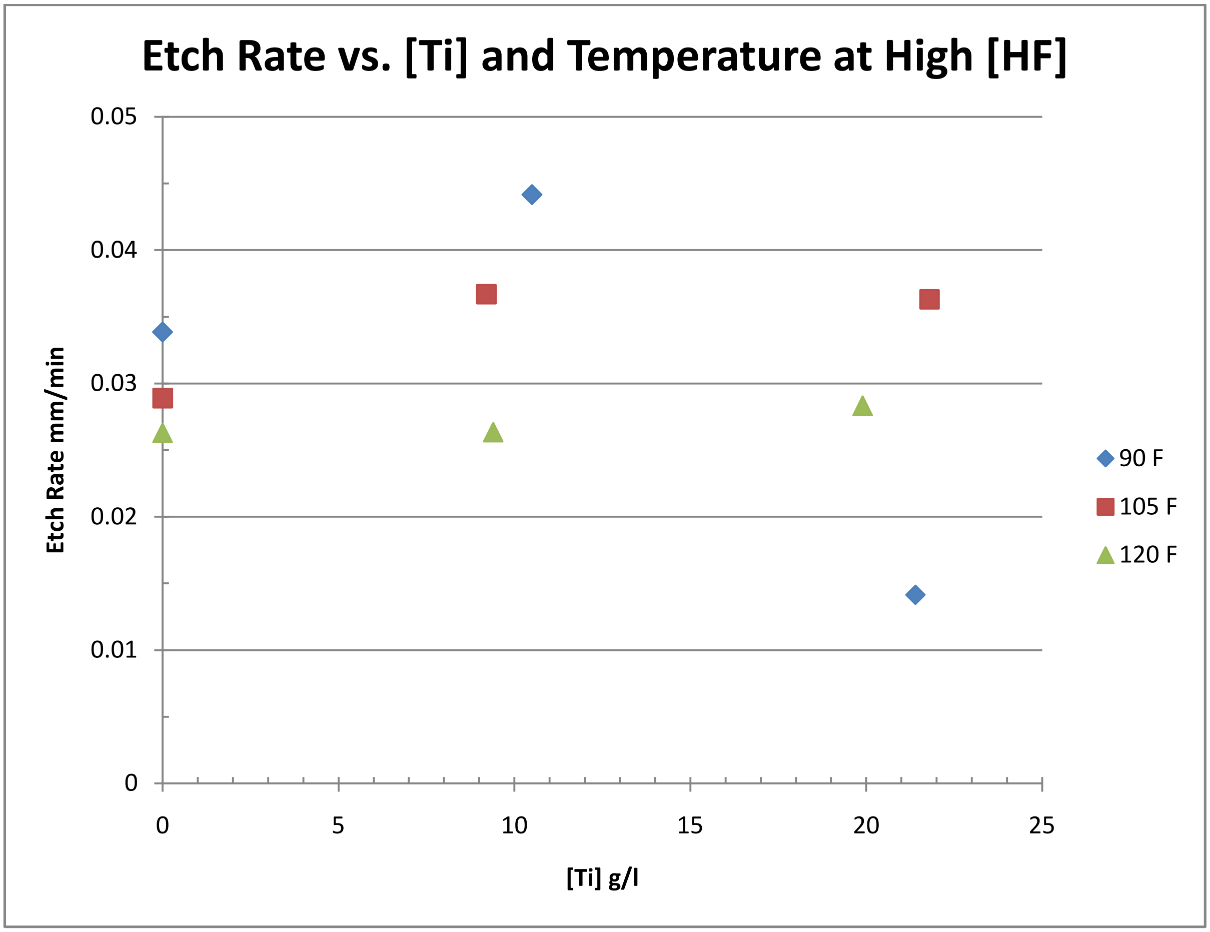

Figure 9: Etch Rate vs. [Ti] and Temperature at High [HF]

4.1.iv Low Temperature

The following figure is a plot of etch rate against [Ti] for the case of low temperature. The figure clearly shows that the etch decreases with an increased titanium concentration for the case of low temperature. For example, in the case of a 9% HF solution, the etch rate falls from .0442 mm/min to .0142 mm/min over a 10g/l change in [Ti].

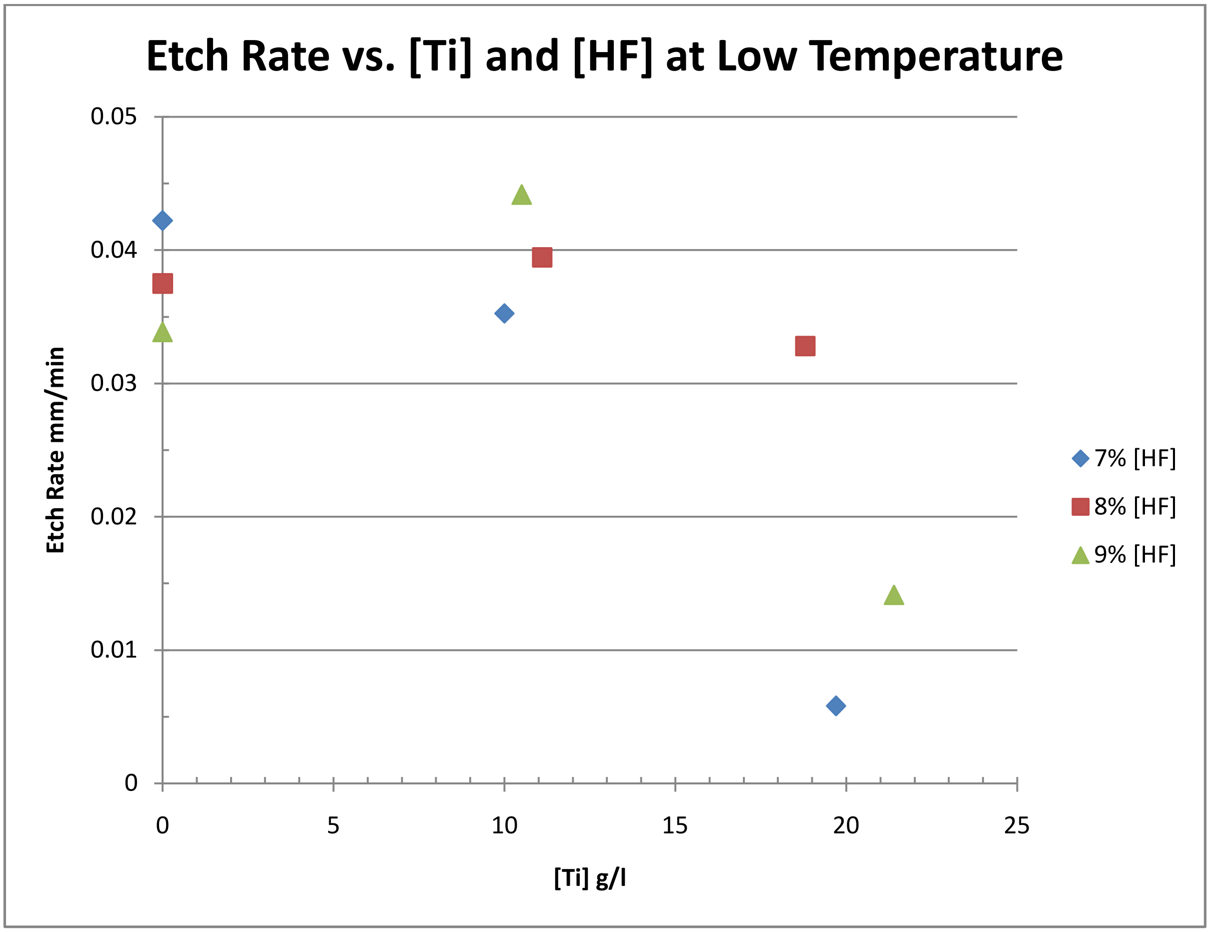

Figure 10: Etch Rate vs. [Ti] and [HF] at Low Temperature

4.1.v High Temperature

The following figure is a plot of etch rate against [HF] for the case of high temperature. The figure clearly shows that the etch decreases with lower acid content. For example, in the case of a 10g/l Ti solution, the etch rate falls from .0314 mm/min to .0216 mm/min over a 1% decrease in [HF].

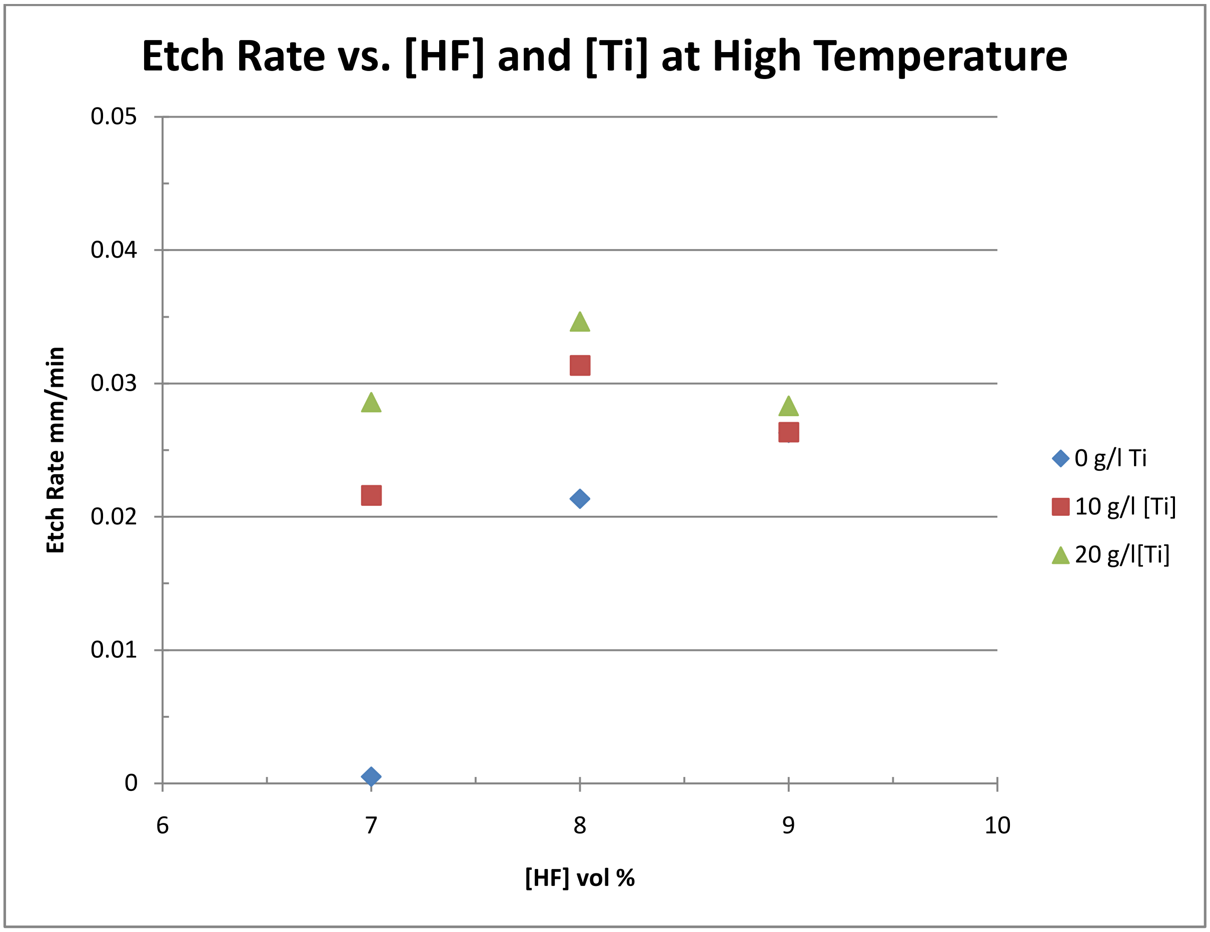

Figure 11: Etch Rate vs. [HF] and [Ti] at High Temperature

4.1.vi Low [HF]

In Figures 12 and 13 the hydrofluoric acid concentrations have been grouped as 7% HF and 8% and 9% HF for higher HF in plots of etch against temperature and [Ti]. The figures clearly shows that at medium to high temperatures and [Ti], the etch rate is relatively lower for low [HF] solutions. For example, in Figure 12, in the case of a 120°F solution, the average etch rate for 7% HF is .0169 mm/min whereas the average etch rate for higher [HF] is .0301 mm/min. A similar analysis will net the same result if conducted with the data from Figure 13.

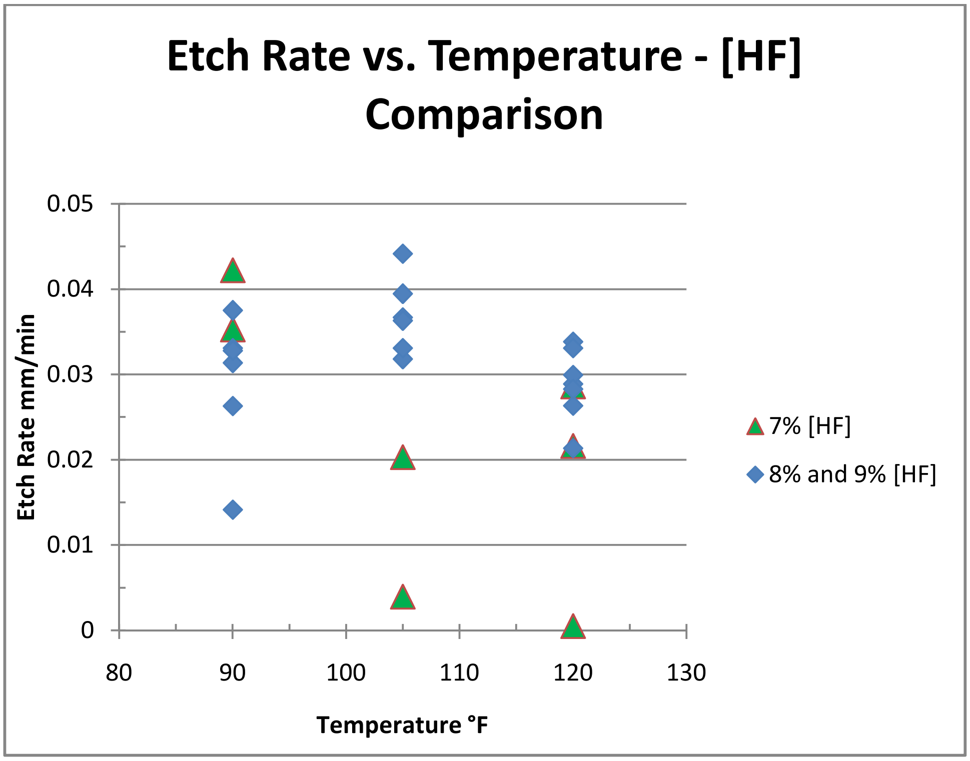

Figure 12: Etch Rate vs. Temperature - [HF] Comparison

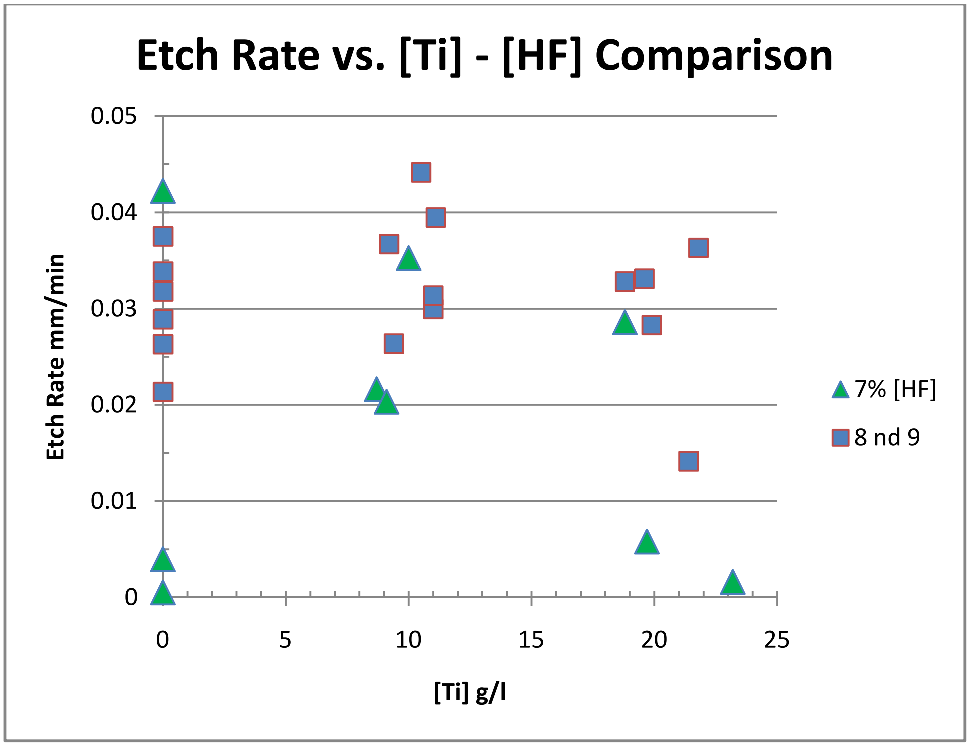

Figure 13: Etch Rate vs. [Ti] - [HF] Comparison

4.1.vii Medium HF

The following figure is a plot of etch rate against temperature for the case of 8% HF. The figure clearly shows that the etch rate is relatively stable with respect to other variables. What is most striking about this set of data is the closeness of all the data points with respect to the [Ti] and temperature. For example, the average etch rate for all the data points in this figure is .0324 mm/min. The average etch rate for the three temperatures, 90° F, 105° F and 120° F are respectively, .0366 mm/min, .0316 mm/min, and .0291 mm/min.

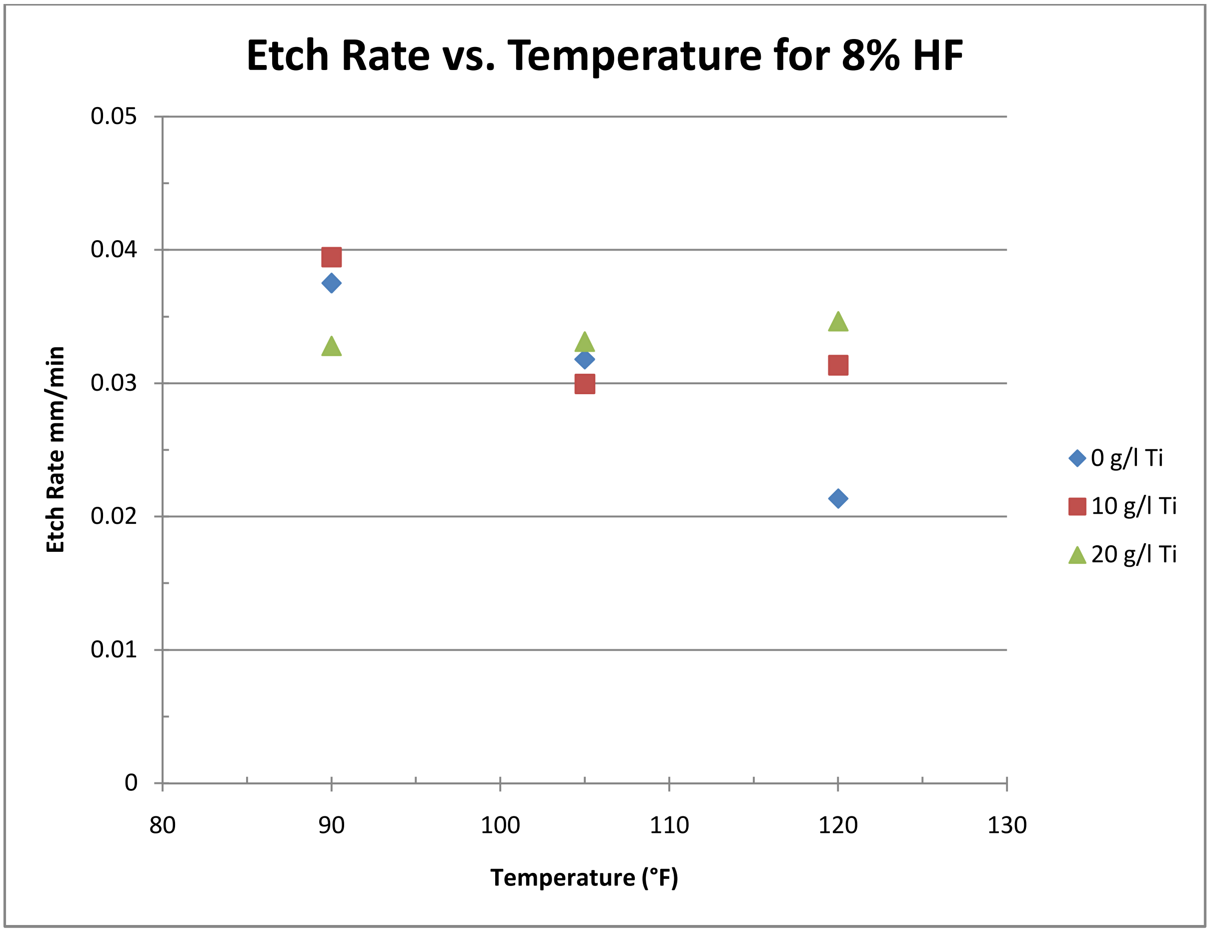

Figure 14: Etch Rate vs. Temperature for 8% HF

4.2 Sources of Error

Our experimentation generated several sources of error. First, the cooling water apparatus that was used to surround the simulated chemical milling bath, may have created some abnormal temperature patterns, thus affecting the data collected. For example, in Figure 8 the data point for 7% HF and 105°F should be higher to support the trends of the remaining data. Secondly, the evaporation of nitric and hydrofluoric acid may have caused irregularities in the measured concentrations of each. Lastly, the small number of data points renders the observations less reliable.

Future experimentation could be improved by taking these sources error into account. Changes to the apparatus may eliminate interference of the cooling water and minimize evaporation. Additionally, increasing the number of trials for each set of conditions would allow for greater reliability.

5. Conclusions & Recommendations

5.1 Avenues of improvement for Chemical Milling process at Wyman-Gordon

5.1.1 Improve control scheme

We recommend that WG improve their control scheme for the chemical milling process in two ways. First, by developing a more comprehensive understanding of the process, WG will be able to utilize both time and raw materials more effectively. Secondly, with automation, WG can insure that the process is running under optimal conditions. By using a set point of 8% HF, for all temperatures 90°F-120°F, a given part will be etched most effectively.

5.1.2 Optimization of Process by Data Gathering and Procedural Change

The use of acid solutions to remove a layer of materiel from a forged metal alloy is, in essence, a fairly simple process. It does not require a tremendous amount of technical knowledge, nor does it necessitate a comprehensive chemical understanding of the exact parameters of the process.

This chemical knowledge is of incredible use, however, in the mission of optimizing the process. Optimization of a process requires either a theoretical model or an empirical model which can be analyzed – and optimized. Due to the diverse types of alloys in the forgings processed in the hydrofluoric-nitric bath and the ever changing conditions of the bath on a daily, or even hourly, basis, no experimental program could be developed that would not be prohibitively laborious and expensive, and still result in a comprehensive understanding of the process in an actual useful way.

That is not to say, however, that this information is unattainable. On a daily basis, technicians utilize the bath with a wide variety of forged alloys, in a wide variety of conditions. They put the forgings into the bath for a set, and recorded, amount of time, and they measure the amount of alloy removed. Furthermore, a temperature readout is located where the technician operates the equipment during milling, so the temperature is also a readily available piece of data. These are three of the most important data needed to optimize the process. The final pieces of data that would be needed to have a fairly complete empirical knowledge of the process are the real time acid concentrations and the titanium concentration. Utilization of the equipment recommended above would supply these values. Thus an empirical model of the dependency of the etch rate on the different variables of interest could be developed simply by accurate and record keeping.

As each bath preparation can dissolve a finite amount of titanium before it must be replaced preventing overmilling of a part is a clear way to reduce costs. If we define the productive use of a bath by the thousandths of an inches it can mill in a single preparation lifetime (using a unit area), then each thousandth of an inch of over milling represents a loss of productivity of the bath. This in turn means an increase in cost of the process. This increase is realized in both the dumping costs and the solution preparation costs. During one of my occasions of observing the process being performed by a technician, the ultimate result of the milling was two thousandths more than the requisite fifteen thousandths quality requirement. This was seen by all involved as a “success” for the quality specification was met. If this was a standard occurrence, and it is, based upon the lack of any procedure to *prevent* overmilling, over the lifetime of the bath it represented a loss of productivity of the bath by nearly 12%.

If a comprehensive empirical model of the operation of the bath was developed it could lead to a procedure whereby a technician is given a readout by a computer of the exact amount of time the forging of interest should be milled based upon real-time conditions of the bath. All that would be left to do is for the technician to confirm (as is already the procedure) that the quality specification has been met. Thus, the ultimate procedure for a technician would only be made simpler in the long run, and the increased

5.1.3 Reclaim end of lifecycle acid waste for recycling

WG overall goal with respect to the chemical milling process is cost savings. Approximately 80% of the material in the chemical milling process leaves the plant as waste. By reclaiming these materials, WG can minimize the amount of raw material it needs to purchase. Furthermore, this will allow WG to reduce its contribution to hazardous waste landfills.

5.1.4 Prevent evaporation through tank retrofit or other means

A significant amount of both hydrofluoric acid and nitric acid are lost from the chemical milling bath via evaporation. These losses could be mitigated by further investigation into preventative measures such as floating media, tank cover design, and optimal cooling and heating cycles. These improvements may ultimately provide cost savings via raw material purchasing and waste reduction.

5.1.5 Change milling acid

There has been previous research in the area of chemical milling acid alternatives. fluoroboric acid was shown to achieve comparable etch rates to hydrofluoric acid. In addition, it was shown that hydrogen embrittlement does not occur in the presence of fluoroboric acid. Although the per gram cost of fluoroboric acid cost is greater than that of hydrofluoric and Nitric acids, in operation the use of fluoroboric acid was shown to be significantly less expensive.

5.2 Recommendation for Further Projects

From our research efforts and the efforts of previous projects, we have concluded that the following list represents the highest priority of research projects for WG to pursue. We recommend that future project groups explore the following research avenues:

- Design an on-site acid reclamation unit (Distillation)
- Develop a model of the chemistry in the process to assist in determining optimum operating conditions of the bath and proper procedure for its maintenance
- Investigate the options available to prevent needless evaporation from the acid baths
- Investigate the chemical and economic feasibility of utilizing automation in the control scheme
- Investigate the chemical and economic feasibility of utilizing a different acid etchant

A continuing mission to understand and subsequently improve the chemical milling process utilized by Wyman Gordon will result in higher quality and lower cost.

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7. Appendix

7.1 HF Experiment Data Sheet

Temp. (° F)	[HF] (g/l)	[Ti] (g/l)	Time (min.)	Initial Temp. (°C)	Final Temp (°C)	Initial thickness (m)	Final thickness (m)	Etch rate1 (g/min)	Etch rate 2 (g/min)
90	7	0							
105	7	0							
120	7	0							
90	7	10							
105	7	10							
120	7	10							
90	7	20							
105	7	20							
120	7	20							
90	8	0							
105	8	0							
120	8	0							
90	8	10							
105	8	10							
120	8	10							

90	**8**	**20**							
105	**8**	**20**							
120	**8**	**20**							
90	**9**	**0**							
105	**9**	**0**							
120	**9**	**0**							
90	**9**	**10**							
105	**9**	**10**							
120	**9**	**10**							
90	**9**	**20**							
105	**9**	**20**							
120	**9**	**20**							

7.2 HF Experimental Data

Test Piece	T_0	[HF]	[HF] final	[HNO3] final	[Ti] goal	[Ti] initial	[Ti] final	Bath Vol (ml)	$t_{1\&}t_2$	T_1	T_2	l_0 (mm)	l_1 (mm)	l_2 (mm)	$Etch_1$ (mm/min)	$Etch_2$ (mm/min)
	(° F)	(vol %)	(vol %)	(vol %)	(g/l)	(g/l)	(g/l)		(min.)	(°C)	(°C)					
1	90	7			0	0		500	2 & 10	39	90	25.548	25.407	24.675	0.03525	0.0366
1	105	7			0	0		500	2 & 10	38	38	24.675	24.652	24.618	0.00575	0.0017
1	120	7			0	0		500	2 & 10	53	65	24.618	24.579	24.472	0.00975	0.00535
2	90	7	3.9	10.1	0	0	19	500	2 & 10	38	97	25.47	25.416	24.572	0.0135	0.0422
2	105	7	2.9	8.2	0	0	20.1	500	2 & 10	44	52	24.572	24.534	24.455	0.0095	0.00395
2	120	7	3	8.2	0	0	21.9	500	2 & 10	48	48	24.455	24.431	24.421	0.006	0.0005
3	90	7	2.66	7.08	10	10	28.4	300	2 & 10	35	96	25.336	25.287	24.582	0.01225	0.03525
4	105	7	2.92	7.17	10	9.1	27.2	300	2 & 10	45	62	25.329	25.29	24.884	0.00975	0.0203
6	120	7	3.32	6.68	10	8.7	28	300	2 & 10	56	90	25.279	25.229	24.797	0.0125	0.0216
7	90	7	4.1	8.75	20	19.7	37	300	2 & 10	35	50	25.294	25.257	25.141	0.00925	0.0058
14b	105	7	4.23	7.39	20	23.2	42	300	2 & 10	38	41	25.271	25.248	25.216	0.00575	0.0016
5	120	7	4.4	6.09	20	18.8	40	300	2 & 10	60	92	25.076	24.965	24.393	0.02775	0.0286
8	90	8	4.62	5.4	0	0	34	300	2 & 10	47	84	25.387	25.335	24.585	0.013	0.0375
9	105	8	4.15	5.7	0	0	35	300	2 & 10	52	87	25.376	25.305	24.669	0.01775	0.0318
10	120	8	4.76	4.42	0	0	34	300	2 & 10	104	92	25.563	25.265	24.838	0.0745	0.02135
14a	90	8	5.96	4.03	10	11.1	47	300	2 & 10	41	86	25.218	25.152	24.363	0.0165	0.03945
16	105	8	6.82	4.52	10	11	54	300	2 & 10	70	70	24.588	24.421	23.822	0.04175	0.02995
17	120	8	5.2	4.82	10	11	57	300	2 & 10	90	73	24.587	24.28	23.653	0.07675	0.03135
18	90	8	5.71	5.8	20	18.8	54	300	2 & 10	38	84	25.526	25.469	24.813	0.01425	0.0328
15	105	8	5.45	5.21	20	19.6	56	300	2 & 10	52	85	25.27	25.195	24.533	0.01875	0.0331
19	120	8	6.61	5.8	20	23.3	60	300	2 & 10	52	90	25.482	25.438	24.745	0.011	0.03465
11	90	9	4.35	5.7	0	0	41	300	2 & 10	59	89	25.453	25.428	24.751	0.00625	0.03385
12	105	9	5.23	4.62	0	0	43	300	2 & 10	97	81	25.4	25.163	24.585	0.05925	0.0289
13	120	9	4.97	5.01	0	0	42	300	2 & 10	99	84	25.384	25.048	24.522	0.084	0.0263
20	90	9	6.64	3.83	10	10.5	64	300	2 & 10	57	80	25.29	25.189	24.306	0.02525	0.04415
21	105	9	6.63	4.23	10	9.2	62	300	2 & 10	70	77	25.31	25.125	24.391	0.04625	0.0367
23	120	9	7.66	4.03	10	9.4	60	300	2 & 10	109	73	25.321	25.044	24.517	0.06925	0.02635
25	90	9	5.15	6.98	20	21.4	37	300	2 & 10	34	77	25.274	25.237	24.954	0.00925	0.01415
24	105	9	7.25	4.82	20	21.8	64	300	2 & 10	60	90	25.239	25.179	24.453	0.015	0.0363
22	120	9	7.79	3.83	20	19.9	74	300	2 & 10	100	76	25.364	25.112	24.546	0.063	0.0283