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CHEMICAL MILLING AND THE REMOVAL OF ALPHA CASE

A Major Qualifying Project Report:
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by

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Abstract

Wyman-Gordon is currently attempting to more accurately measure metal removal rates of chemically milled pieces, optimize acid bath life, and determine any trends between the two. Accurately determining metal removal rates would result in a more efficient and less time consuming chemical milling process. Based on results, it was determined that alpha case plus the titanium alloy is removed during chemical milling. An optimized and more efficient bath would lead to less waste acid, thereby reducing environmental impacts, and enhanced production quality potentially resulting in increased revenue and decreased process costs.

Acknowledgements

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Executive Summary

Wyman-Gordon is a manufacturing company that specializes in titanium and steel aerospace parts. Titanium alloys, in particular, are ideal for the aerospace industry due to their high strength to weight ratio. However, titanium is not the easiest metal to forge. Incredibly high temperatures and pressures are required to produce final products. Furthermore, heating and forging are not the only steps in the complete process. Chemical milling must be used as well to finalize products. The milling step removes a brittle alpha case which develops when heating in the presence of oxygen. Alpha case is more prone to cracking and therefore must be removed so that quality aerospace standards are met.

The chemical milling process is an imprecise science that employs the use of powerful acids. The process is relatively inefficient, expensive, and can be harmful to the environment. Having an increased knowledge of titanium alloy chemical milling will provide many benefits. Currently the length of time which a piece is dipped in acid is approximated based on trial and error over many years. Knowing exactly how long each piece must be milled for to remove the appropriate amount of metal will enhance production quality and increase the efficiency and life time of the acid bath. Increasing the bath life in turn lowers costs as less acid will have to be purchased, delivered, and disposed of. Furthermore, this would also decrease the environmental impact of the chemical milling process.

The goal of this project was to investigate the current chemical milling process used by Wyman-Gordon and study the effects it has on the most commonly used titanium alloys, Ti-6V-4Al and Ti-6V-4Al ELI. The primary intention of this was to discover the metal removal rate based on the acid and titanium concentrations of the acid bath and varied dip time methods. A secondary goal of this project was to analyze various measurement techniques, such as feeler gauges and weight comparisons, to determine how much metal has been removed via milling. Lastly, a comparison was made to determine if there was a difference in the amount of metal removed from the pieces that did and did not have alpha case.

To perform the necessary experiments to complete this project, an appropriate number of titanium alloy test pieces and acid bath samples were collected. Forty, approximately one inch cube, test pieces of each alloy type were obtained. Half of these went through a similar heating process which most forged titanium parts experience to develop alpha case. Additionally, ten acid bath samples were acquired over the course of the general use of Wyman-Gordon's main

acid tank to ensure a typical concentration profile of the entire life of the acid bath. It is known that as the titanium concentration of the acid increases, the metal removal rate decreases. Previous studies have been done which tested the use of different acids and the possibility of precipitating titanium out of the solution to alleviate this problem. This study was more focused on the current process used by Wyman-Gordon in which a hydrofluoric and nitric acid solution is used.

The experimental procedure developed for this project relied on the consistency of testing to provide accurate results. Each bath sample was used to test eight different test pieces: two heated with alpha case and two non-heated pieces of each alloy type. One of each type was tested for one time interval and the other for a different time interval. The acid bath being tested was contained in a beaker that was kept in an ice bath to regulate the temperature. The test pieces were placed into the acid bath individually with a pair of plastic tongs for the appropriate time, rinsed in water, and then placed back in the acid until the test was complete. This process was followed for all eighty pieces. Both before and after the test pieces were milled, they were weighed to determine the weight change and thus the mass of the metal removed. Another method to measure the amount of metal removed was through the use of feeler gauges, thin precision cut pieces of metal with known thicknesses. Titration data providing the acid and titanium concentrations of each bath sample, collected by Wyman-Gordon, was also recorded for making comparisons with the results.

Most data found was inconclusive due to experimental errors but some assessments could still be made. It was found that the bath's HF concentration was directly correlated to the metal removed by the bath. Although it does not clearly show cause, it can also be seen that the amount metal removed decreases as the titanium concentration increases. Some of the milling times proved to be more effective for one alloy than the other, as well as at different points in the life time of the bath. This is presented in Figure 1 below. When it came to measuring the amount of metal removed, feeler gauges were fairly inaccurate. Weighing the pieces and comparing the weight lost to the exposed surface area proved to be a much more effective way to calculate the metal removal rate.

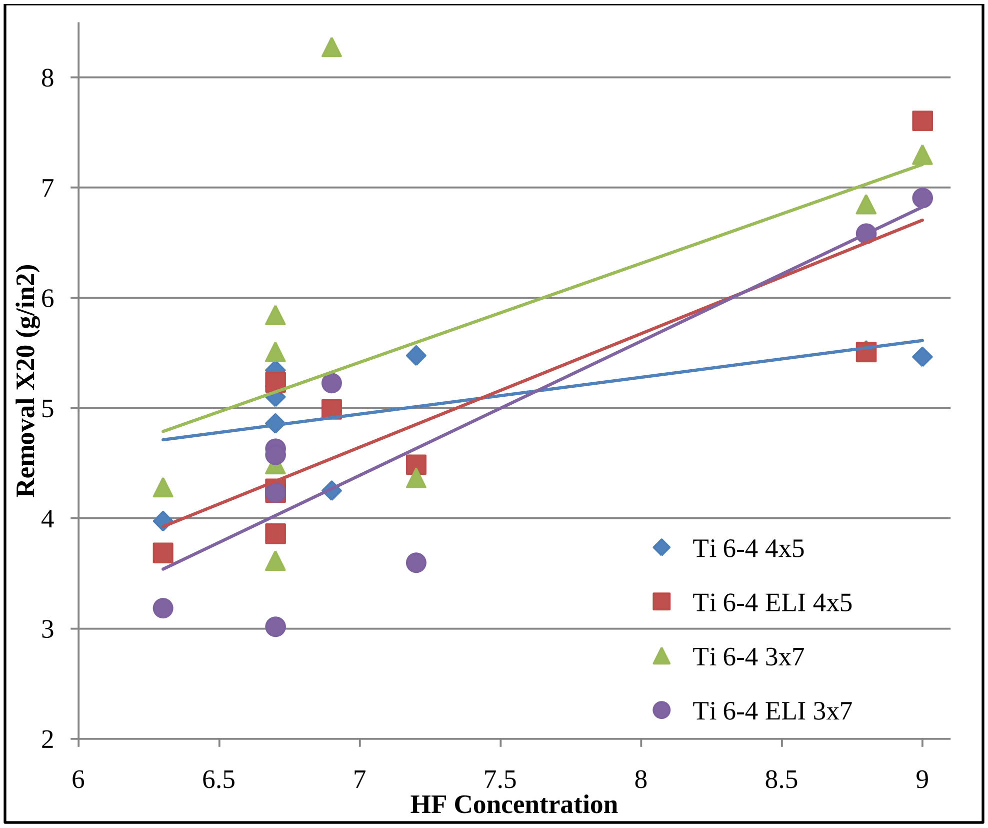

Figure 1: Metal Removal Comparison to HF Concentration

To make more convincing decisions in the future, a more accurate experimental procedure should be followed as proposed and displayed in Appendix C. This could be used to collect further data with regard to titanium concentration and resulting metal removal rates. To ensure that the proper amount of titanium is milled, it would be more precise to use weight measurements opposed to approximations based on human judgment and feeler gauges. This could be done predetermining how much weight needs to be removed according to the surface area, known based on die dimensions, of the part. Lastly, although using acid spikes is relatively effective in prolonging the acid bath life, more research can be done to look into alternatives such as removing titanium from the bath or recycling acid rather than simply disposing of the expended bath.

Chapter One: Introduction

The Wyman-Gordon Company is currently one of the largest manufacturers of forged metal aerospace parts. These parts are primarily used in military and government applications, but Wyman-Gordon also develops parts for general industry uses (Wyman-Gordon, 2009). Parts are forged at high temperatures and pressures which form a brittle surface layer called an alpha case. The alpha case removal process, in which the part is etched using an acid bath in a process known as chemical milling, is necessary to meet aerospace and industry quality standards.

The chemical milling process is not complex, but if done improperly it can become both costly and time consuming. If the piece is not etched correctly, the process can result in the waste of acid, time, or a total loss of the part. Wyman-Gordon is looking to optimize efficiency and cost effectiveness of their chemical milling process. The company has previously researched the problem; however, little has been done to optimize the process due to time constraints on past MQPs and lack of recommendations. (Postale, 2009).

In spite of attempts to improve the chemical milling process, Wyman-Gordon is left with a method that is not entirely efficient. The alpha case buildup on a forged part should be at a minimum thickness to save usable acid and time in the acid bath. The most effective acid bath time needs to be calculated to fully remove the alpha case. The part should not be submerged in acid too long because it would reduce its quality due to hydrogen pickup. Hydrogen pick up is the infusion of hydrogen into a metal surface, which causes metal brittleness and weakness. The metal removal rate must be known to determine the required time spent in the acid (Burham, Dannheim, 1994).

The company does not have a specific technique to measure the amount of alpha case removed after each bath. This causes two issues regarding the quality of the forged part and the life of the acid bath used for etching. Without knowing the etch rate of the bath or the amount of alpha case remaining, it cannot be determined if quality standards are met. Moreover, if the part is left in the acid bath too long, acid is wasted and the life of the bath decreases. The amount of alpha case removed and time submerged in the bath should be determined specifically for the Wyman-Gordon process (Knox, Senft-Grupp, 2009).

Another issue plaguing the Wyman-Gordon process is the lifespan of the acid bath. Currently the bath is periodically spiked with concentrated hydrofluoric acid and/or nitric acid to increase the concentration and prolong the bath life. More frequent spikes are required towards the end of a bath's life to maintain the optimum concentration of acid. This method is not the most effective way to optimize bath life because it would increase hydrogen pickup causing the part to weaken and crack after treatment (Chen, Yu-Lin, 1990).

In the past, there have been several Major Qualifying Projects done at Worcester Polytechnic Institute that involved chemical milling of titanium. A report done by Jeffrey Cayer, Jebediah Ledell, Jocelyn Russo, and Raina Shahbazi discussed how the alpha case formed and developed methods to minimize its formation. Another report determined the optimum etching times for titanium parts (Burham, Dannheim, 1994), while a third provided suggestions for an optimal bath life (Knox, Senft-Grupp, 2009). Supplemental research to that done at Worcester Polytechnic Institute can be found at an online homepage for the Finishing Industry which provides a forum of professional opinions on alpha case removal (finishing.com, 2010). Our Major Qualifying Project will expand upon these ideas and develop and implement solutions for the gaps in previous MQPs research.

We assessed the existing metal removal measurement technique to develop a more accurate method. Using test coupons of various alloys, both with and without alpha case, we compared the amount of titanium removed. Similarly, relationships between titanium and acid concentrations in the bath compared to amount of metal removed were determined. Finally, we determined the optimal bath life based on bath concentration, composition, and cost effectiveness. Satisfying these objectives increased efficiency at Wyman-Gordon by optimizing the process and potentially reducing costs.

Chapter Two: Background

The following chapter explains the necessary background information to understand this project. The information includes Wyman-Gordon history, titanium and its applications, and the chemical milling process.

Wyman-Gordon

The Wyman-Gordon Company was founded in 1883 and prides itself on making high quality forged parts. It uses "best-in-class" forging processes combined with 118 years of experience. Currently, Wyman-Gordon is the leading manufacturer of aerospace parts. They are also a major producer of industrial gas turbine forgings and extruded pipes for power generation and energy applications.

There are manufacturing sites in five countries, with thirteen plants worldwide. The company serves the locomotive, aerospace, power generation, oil and gas exploration, automotive, medical, food processing, and nuclear markets. Specifically in the Grafton site, structural forgings for military and commercial aircraft applications are constructed. The process involves forging titanium, steel, or nickel alloys (Wyman-Gordon, 2009).

Titanium

Titanium was discovered and named in 1791 and 1795, respectively. Its impure form was first prepared in 1887; however, the pure metal (99.9%) was not made until 1910. Titanium is found in a number of places including: meteorites, m-type stars, minerals, iron ores, the ash of coal, plants, and the human body. The method that is still largely used to produce titanium commercially was discovered in 1946 and uses magnesium to reduce titanium tetrachloride and isolate the pure metal. Titanium, when pure, is a lustrous, white metal. It has a low density, good strength, is easily fabricated, and has excellent corrosion resistance. Titanium is important as an alloying agent with other metals. Alloys of titanium are principally used for aircraft and missiles where lightweight strength and ability to withstand extremes of temperature are important (University of California, 2004).

Alloys

Alloys can be classified into three categories:

- Alpha alloys – contain neutral alloying elements and/or alpha stabilizers only and are not heat treatable

- Alpha + Beta alloys – contain a combination of alpha and beta stabilizers and are heat treatable to various degrees
- Beta alloys – metastable and contain sufficient beta stabilizers to completely retain the beta phase upon quenching, and can be solution treated and aged to achieve significant increases in strength (CRS Holdings Inc., 2000)

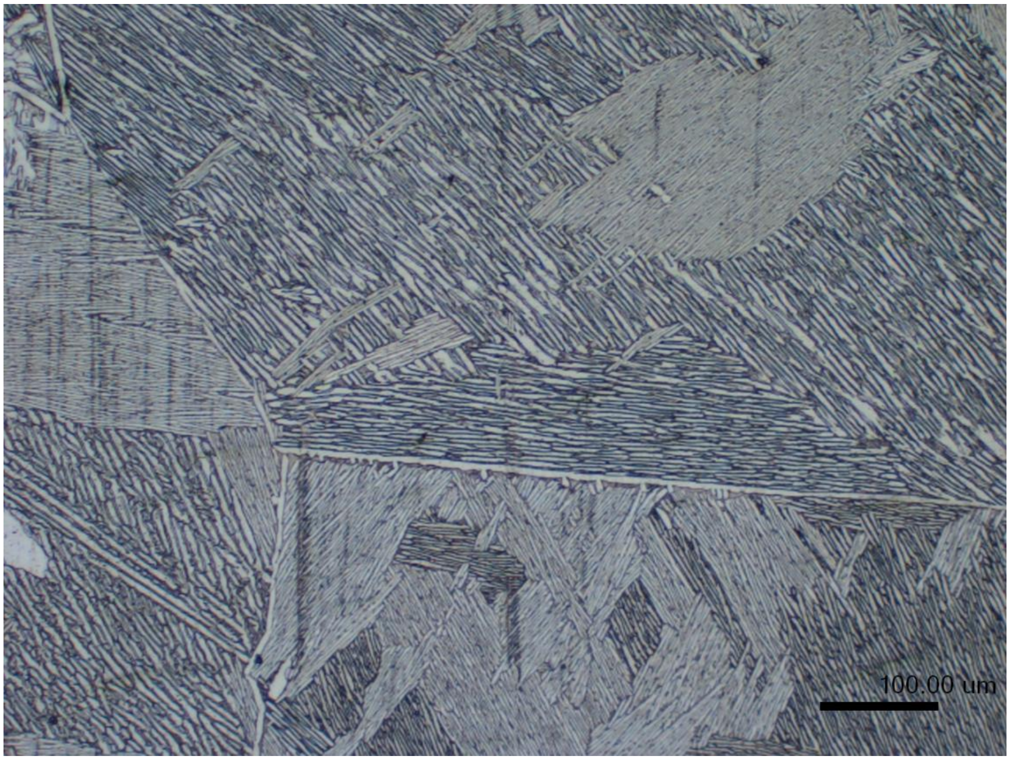

Figure 2: Titanium Microstructure

This figure shows the different alloy phases of titanium. Stabilizers are elements that have high solubility in metals and are typically used in alloys. The purpose of adding stabilizers to titanium is to alter the transformation temperature of a specific phase to create a binary alpha-beta phase. Alpha stabilizers, typically aluminum, are added to raise the transformation temperature of the alpha phase. Vanadium, an isomorphous beta stabilizer, is completely soluble in the beta phase. Other beta stabilizers such as iron are not completely soluble, which produces eutectoid phase. The stabilizers are represented in the name by their periodic table symbols and weight percent. For example, Ti-6Al-4V is 6% aluminum and 4% vanadium.

Formation of Alpha Case

Titanium readily absorbs oxygen at high temperatures, and leads to the formation of alpha case and oxidation. Alpha case is the carbon, nitrogen, or especially oxygen enriched alpha stabilized surface that is present on titanium after forging or heating (Lit Lab Inc, 2010). Figure 3 represents a titanium-oxygen phase diagram. The HCP phase represents the alpha phase and BCC is the beta phase. The alpha-beta phase is the region in between HCP and BCC. The Wyman-Gordon heats their titanium to approximately 1700°F, or approximately 920°C. The line dividing the binary phase from the HCP phase is the concentration of oxygen needed to form alpha case. The heat treatment process at Wyman-Gordon reaches temperatures on the phase diagram where this scenario is possible.

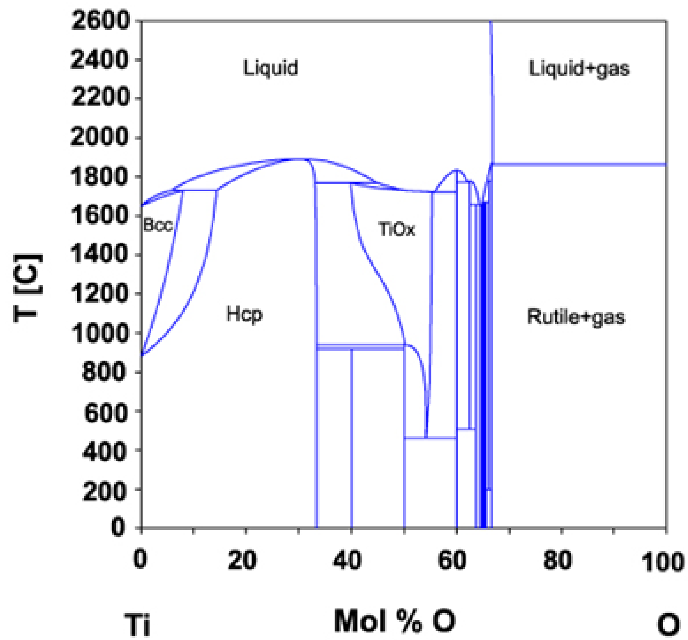

Figure 3: Titanium-Oxygen Phase Diagram (National Institute of Material Science, 2008)

Figure 4 represents oxygen concentration as air reacts with titanium at the surface during the heating process. As expected, the carbon and nitrogen concentrations are low and stable. The oxygen is much more soluble in titanium; therefore its concentration gradient is much higher at the surface. The values presented in the graph below are subject to heating conditions, but the general behavior of oxygen, nitrogen and carbon is typical for titanium forging. The oxygen concentration gradient represents the alpha case phase described above.

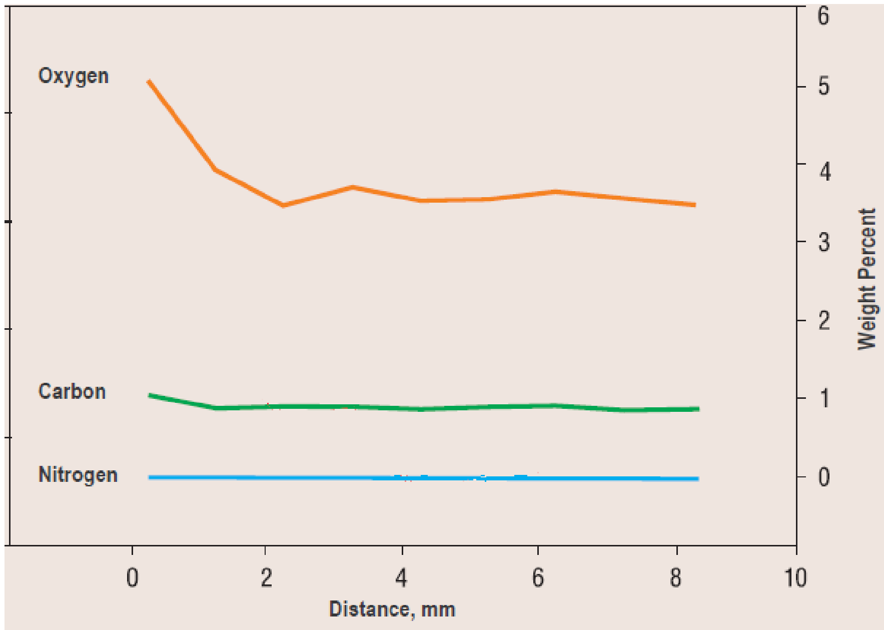

Figure 4: Oxygen Concentration in Titanium (Microstructure of Titanium Welds, 2004)

Alpha case is a definite drawback to titanium usage as it can affect fatigue strength, corrosion resistance, and limits titanium's high temperature capability with respect to mechanical properties. The best ways to minimize alpha case formation are through the use of vacuum metallurgy in which the titanium can be heated and forged in the absence of oxygen. Another way to minimize alpha case formation is through the use of high end ceramic dies during forging, which have a more negative free energy than TiO_2 and draw the reaction caused by the oxygen away from the titanium. Alpha case can also be removed after heat treatment mechanically or chemically.

Ti-6Al-4V

Ti-6Al-4V is the most common Ti alloy and accounts for more than 50% of total titanium usage. It is an alpha + beta alloy, which is heat treatable to achieve moderate increases in strength. Ti-6Al-4V is a world standard in aerospace applications because of its high strength, light weight, ductility, and corrosion resistance. The most common applications of this alloy include: aircraft turbine engine components, aircraft structural components, aerospace fasteners, high-performance automotive parts, marine applications, medical devices, and sports equipment (CRS Holdings Inc., 2000).

Ti-6Al-4V ELI

ELI stands for extra low interstitials and is a higher purity version of Ti-6Al-4V, with lower limits on iron and interstitial elements C and O. Like Ti-6Al-4V, it is also an alpha-beta alloy. TI-6-4 ELI has excellent biocompatibility, and therefore has been the material of choice for many medical and dental applications. It has superior damage tolerance (fracture toughness, fatigue crack growth rate) and better mechanical properties at cryogenic temperatures when compared to standard Ti-6Al-4V. Common applications for TI-6-4 ELI include: joint replacements, bone fixation devices, surgical clips, and cryogenic vessels (Dynamet Holdings Inc, 2010).

Aerospace Applications and Standards

The aerospace industry is the single largest market for titanium products primarily due to the exceptional strength to weight ratio, elevated temperature performance, and corrosion resistance of many titanium alloys (Titanium Industries Inc., 2010). Its applications are most utilized in jet engine and airframe components, and other critical structure parts. The use of titanium and new complex alloys in the industry is an ever expanding and groundbreaking field. Jet engines account for the largest single use of titanium, which can be anywhere from 20-30% by dry weight titanium alloy. In the airframes, titanium still competes with other metal alloys such as aluminum, nickel, and iron. Titanium's basic attributes, such as high reliability during performance and good corrosion resistance, make it a top choice for use in engines and airframes. It is also used in space shuttle applications for a larger section size. Thick section titanium or heavy section size is generally defined as forged or rolled thickness that exceeds four inches These titanium alloys, Ti-6Al-4V and Ti-6Al-4V ELI, for a given process and heat treatment, demonstrate superior fatigue and fracture toughness properties from the standpoint of uniformity through the entire heavy section thickness.

Minimum tensile properties for Ti-6Al-4V and Ti-6Al-4V ELI are summarized in Table 1. These properties meet military requirements for aircraft quality unless the customer specifies otherwise (Department of Defense, 1986).

Table 1: Aerospace Mechanical Standards

Alloy	Thickness (In.)	Width (In.)	Tensile Strength (ksi)	Yield Strenth at 0.2% Offset (ksi)	Percent Elongation
6Al-4V	4.00 and under	48 max	130	120	10
6Al-4V ELI	1.5 and under	16 max	130	120	10

Chemical Milling

Chemical milling processes are often used on engine parts to create thin cross-sections and very smooth surface finishes as opposed to machining. This is achieved by the selective or overall removal of large amounts of metal through chemical dissolution. In the typical chemical milling process, the part is submerged in the milling solution which is then agitated to continuously present a fresh layer of solution on the surface of the part and ensuring a uniform metal removal. Popular milling solutions involve the use of hydrofluoric acid in concentrations anywhere from 1-10%. Most dilute or organic solutions will not etch the titanium. The goals of chemical milling are to: substantially eliminate hydrogen at the metal's surface, obtain a high metal removal rate, produce smooth bright finishes, and be compatible with photoresist-type masks commonly used in the selective milling of titanium (Chemical Milling of Titanium, 2010).

HF/Nitric Acid Solution

Hydrofluoric and nitric acids are most commonly used to etch titanium alloys because they form a highly acidic solution. The stronger the acid, the more metal removed. Due to the dangers of handling and transporting a strong acid, it is more expensive to properly dispose of HF than other weaker acids. A few alternatives to HF are: fluoroboric acid (HBF_4), copper sulfate pentahydrate ($CuSO4{\cdot}5H2O$), ammonium persulfate ($(NH_4)_2S_2O_8$), and sodium fluoride (NaF). Fluoroboric acid and copper sulfate pentahydrate were tested in a previous Wyman-Gordon MQP (Cayer, 1997). The fluoroboric acid had an etch rate approximately 80% of HF's etch rate and the copper sulfate pentahydrate was about 30%. The benefit of using HBF_4 is that the acid does not cause hydrogen embrittlement. On the other hand, HBF_4 is more expensive per gram than HF (Gumbelevicius, 1974). These acids are not as strong as HF and have slower etch rates, but are safer alternatives.

Hydrogen Embrittlement

One major consequence of etching titanium in an acid solution is hydrogen embrittlement, which is the result of hydrogen pickup. Titanium has a high affinity for hydrogen, and it is almost impossible to prevent during etching. Free standing hydrogen in the bath is produced when there is a reaction between the acid and the surface of the titanium. To balance the reaction occurring, the titanium surface picks up positively charged hydrogen ions. The hydrogen molecules coat the surface of the titanium which is called hydrogen pickup. The effect of hydrogen pickup is embrittlement, which is the weakening of the titanium. Embrittlement causes stress and tensile failures which deem the metal part dangerous and unusable (Finishing.com, 2010).

Efficiency of Bath

The efficiency of the bath, or the ability to etch effectively, depends on the concentration of acid, temperature of reaction, and amount of metal dissolved in acid. The greater the concentration of the acid and the higher the temperature, the more the removal rate is accelerated (Cayer, 1997).

The efficiency of the acid bath is vital for proper etching. As the concentration of titanium increases in the bath, the reaction proceeds slower. This is because one titanium ion reacts with six fluoride ions. Approximately twelve grams per liter of titanium will require ten to twenty times longer than one gram per liter of titanium to achieve the same etching (Titanium Recast Layer/Alpha Case Removal, 2010).

Dissolving titanium depends largely on the concentrations of HF and HNO_3. The process contains two stages: active and passive. In the first stage, there is gaseous hydrogen embrittlement. The passive stage incorporates surface strength. The stages are distinguishable, such that damages to the surface can be prevented (Titanium Chemistry in HF and HNO_3 Chemical Milling, 2010).

To combat the increasing titanium concentration, periodic additions of hydrofluoric acid can be made to the bath. It is recommended that the nitric strength remain fourteen times greater than the hydrofluoric acid concentration (Titanium Recast Layer/Alpha Case Removal, 2010).

Safety

Handling hydrofluoric acid entails many safety precautions. It is a corrosive and difficult to handle substance. As a contact poison, it can affect nerve function, and cause cardiac arrest if it enters the blood stream. Due to the low dissociation constant, hydrofluoric acid penetrates quickly. This increases the aforementioned risks.

Nitric acid, on the contrary, is a less dangerous acid. Reactions with nitric acid, such as cyanides and carbides, can be explosive. Other chemicals, such as turpentine, are volatile and can be self-igniting. It must be stored away from bases and organics.   When nitric acid comes in contact with the skin, it turns the skin yellow (HF, 2010).

The acid from the bath can be very harmful to the environment. The fluoride from HF can react with the soil and damage surrounding plants and ecosytems (Environmental Health and Safety, 2010). Nitric acid, on the contrary, neutralizes in the soil.   However, nitric acid in the atmosphere can lead to acid rain (Health Protection Agency, 2010). To avoid these issues and any contamination to the environment, all waste acid must be sent to an appropriate incinerator or disposed in an approved waste facility.

Chapter Three: Methodology

The goals of this project were to assess the existing chemical milling procedure used for Wyman-Gordon's hydrofluoric acid bath, analyze the metal removal measurement technique, and to provide recommendations for process optimization. Using test coupons of various titanium alloys, both with and without alpha case created by heating, we compared the amount of titanium removed and determined correlations between the metal removed and the concentration of acids and titanium in the bath. We analyzed an optimal bath life based on our findings. These goals were developed based on expectations of Wyman-Gordon employees, including Briant Cormier and Brian Postale, the analysis of Wyman-Gordon's procedures, and research on chemical milling practices

Methods for Studying Chemical Milling Metal Removal

To analyze the metal removal, we performed experiments at Wyman-Gordon using acid solutions from a full bath cycle of the K-Tank, Wyman-Gordon's principle acid bath.

Equipment

To perform this experiment, 1500mL samples of hydrofluoric acid were gathered daily from the K-Tank over a two week period for testing eighty Ti test coupons individually. The acid was held in a 400mL glass beaker, which sat in a 2000mL glass beaker acting as an ice bath with a magnetic stirrer. A 600mL beaker was used to rinse the pieces after they were dipped into the acid bath.

A specific list of equipment is:

- Fume hood
- Protective lab coat, gloves, and glasses
- 400mL glass testing beaker
- 2000mL glass ice bath beaker
- 600mL glass rinse beaker
- Lab Journal
- Duct Tape
- Ruler
- 80 Ti test coupons (20 Ti-6-4, 20 heated Ti-6-4, 20 Ti-6-4-ELI, 20 heated Ti-6-4-ELI)
- Magnetic stirrer

- Magnetic stir plate
- Plastic air hose
- Plastic tongs
- Ice
- Thermometer
- Acid solution (H_20, HF, HNO_3)

Test Coupon Preparation

Eighty titanium pieces were obtained and cut into approximate one inch cubes at Wyman-Gordon. To keep each titanium coupon separate, every piece was stored in its own numbered plastic bag. Before experimentation, half of the titanium test coupons had to go through the heating process used by Wyman-Gordon when forging their products. This was done to create the alpha case layer which is formed when the metal is heated. Forty of the eighty total pieces were placed in a laboratory furnace at 1700°F for four hours in Wyman-Gordon's heat treatment department. The pieces were then removed and left to air cool on a metal rack which took approximately one hour. However, alpha case is not the only layer that is formed on the pieces from heating, an oxide scale also formed. Wyman-Gordon removes this scale in a large chamber where they blast the titanium with steel shot. This would have destroyed the smaller test pieces being used for this experiment. Alternatively, a smaller 100 psi sand blasting chamber was used in Wyman-Gordon's research building. All heated pieces were blasted on each side until a visual analysis could confirm that there was no scale and only alpha case left.

Furthermore, all eighty pieces, heated and non-heated, were weighed at WPI in preparation of being weighed again after chemical milling to determine how much metal was removed. As another metal removal measurement technique, duct tape was placed on half of four faces to allow for a feeler gauge to be used to feel how much metal was removed. The surface area left uncovered by the duct tape was measured to be used for calculating the mass per area metal removal. At this point, all of the pieces were ready to be tested.

Experimental Procedure

The setup for this experiment first required preparing the testing area in the fume hood at Wyman-Gordon's chemical lab and wearing the appropriate personal protective equipment. Approximately 175mL of acid from the current day of the cycle was poured into the 400mL glass test beaker. This beaker was placed in the larger glass ice bath beaker with a magnetic stirrer to ensure uniform cooling. The test piece was then placed gently into the beaker using plastic tongs. After the piece has been submerged for the appropriate test time, it was removed and placed in the rinse water beaker and allowed to cool. This process was repeated for the designated time intervals until completion. The pieces were then returned to WPI, where they were weighed again. Four pieces were machined, heated, and examined under a microscope to determine how much metal, alpha case or otherwise, had been formed during the heating process at WPI. These pieces were used for post experimental analysis of alpha case thickness by microscopy. Using an air hose for agitation in the acid bath was discussed but not originally used because of complications at Wyman-Gordon with the air supply. Knowing the effect that it may have had, agitation was used for one day of the bath cycle for comparison purposes.

Figure 5: Experiment Setup with Acid Samples

These experiments were conducted on two separate alloys, Ti-6Al-4V and Ti-6Al-4V ELI, both with and without alpha case, and varying dip times in the bath. The two dip procedures will consist of four dips for five minutes each and three dips for seven minutes each. Focus was on any correlations between dip time and metal removal. Dip times were based around typical procedures followed by Wyman-Gordon for current production.

The following is a step by step layout of the procedure:

1. Wear the proper PPE (lab coat, gloves, and glasses)
2. Clean and set up the fume hood for experimentation.
3. Prepare ice bath with approximately 800mL of water/ice in 2000mL beaker.
4. Fill rinse beaker (600mL) with water.
5. Fill 400mL test beaker with approximately 150-200mL of acid.
6. Wrap duct tape around one half of cube (cover half of one face and continue around to cover half of 4 total faces)
7. Measure the surface area of the non-taped sections of the Ti piece.
8. Using plastic tongs, gently place Ti piece into the acid test beaker.
9. Wait and observe the experiment for the given time (5 or 7 minutes).
10. Remove from acid, allow excess to drip momentarily then dip the piece in the rinse bath for approximately 30 seconds.
11. Repeat steps 8-10 for the appropriate number of dips (3 or 4 depending on dipping time).
12. Rinse the Ti piece thoroughly and return it to the proper bag.
13. Record observations and clean all equipment and the test area.

Data Collection

The table that was used to record data can be found in the Appendix A.

Methods for Developing Optimization Recommendations

To optimize the acid baths at Wyman-Gordon, we studied past and existing acid bath procedures. We reviewed past MQPs, analyzed Wyman-Gordon's suggestions, and researched acid bath methods at other facilities. This involved discussing the bath procedure with Wyman-Gordon employees, and examining other techniques, such as those referred to on finishing.com.

Chapter Four: Results and Discussion

This chapter analyzes the experimental data and its associated trends and errors. The goals of the project were to determine the metal removal in relationship to acid and titanium concentrations in the acid bath and analyze various metal removal measurement techniques. Comparisons were also made between pieces that did and did not have alpha case.

Experimental Analysis

The goal of the experimentation was to maintain a uniform testing scenario in which the various titanium alloy pieces could be milled in an identical fashion for two different time conditions. Doing this minimized variables and the data would therefore be more accurate and more easily compared. Prior to experimentation, this procedure had been satisfactorily composed according to the data available. In hind sight this may not have been the case.

One of the first issues noticed was the lack of uniformity in the test pieces. Most pieces were relatively close to one inch cubes, but a fair amount varied in size substantially. This led to each piece having a different surface area, an important reaction factor. Although surface area was measured individually for each piece, this still added an extra unnecessary variable to the experiment which could cause inconsistent metal removal, one of the key components being measured.

When placing the test pieces in the sample acid baths, there was no consistency or recording of the orientation of each piece. Since the pieces were placed on the bottom of the bath touching the beaker, the surface in contact with the beaker may have had a lower removal than if the piece were suspended. Furthermore, the lack of consistency could lead to some pieces being affected by this issue more than others. Four faces of each piece were half covered by tape, which should have resisted chemical milling on that portion. Therefore, depending on which face was in contact with the beaker, it experienced reduced or no surface reaction.

Another issue arose with the use of duct tape as a milling preventative in order to produce a smooth edge to be measured via feeler gauge. Duct tape was not reliable in terms of remaining fully intact with the test pieces. This added more inaccuracy to the results because the measured weight removal per surface area was based on the surface area that was not covered by duct tape. In some cases the tape allowed acid between itself and the titanium. This allowed more metal removal than expected.

Temperature also plays a role in metal removal caused by the titanium and acid reaction. Per the experimental procedure, an ice bath was used to maintain a limited temperature range and avoid over heating from the exothermal reaction. Temperatures were only taken periodically throughout testing to get an idea of the average temperature. As seen on the one day in which ice could not be used for pieces 8, 28, 48, 68, the presumed increase in temperature had a substantial impact on the metal removed from those pieces. Setting a certain temperature to be tested and that is monitored closely would most likely lead to much more accurate results. This is seen with Wyman-Gordon's set up of a heat exchanger surrounding the acid tank.

Lastly, one of the most outstanding issues realized was the lack of bath agitation. Wyman-Gordon uses extensive agitation in their current process as it has proved to increase metal removal due to reaction greatly. This is due to the increased titanium concentration, which slows reaction, at the surface of the reaction when agitation is not used. There was not a proper agitation set up available in the facilities and due to the lack of time, alternatives could not be considered. Using agitation would have provided more accurate results that were more representative of the actual process being used by Wyman-Gordon.

Metal Removal and Measurement Technique

As was anticipated, the feeler gauge method for measuring metal removal did not prove accurate. The feeler gauge graphs, although individually did not reveal many trends, supported conclusions reached through other methods of analysis. Comparing the graphs of Ti-6-4 and Ti-6-4 ELI revealed, during the three by seven minute time frame for both heated and non-heated pieces that the Ti-6-4 pieces appear to have more metal removed than the TI-6-4 ELI pieces. However, the four by five minute time frame favored the TI-6-4 ELI pieces. Comparing the heated vs. non-heated data revealed that the Ti pieces with alpha case had less metal removed than those without. Finally, the Ti-6-4-ELI heated pieces were the least affected by chemical milling and it appears that the four by five minute time frame leads to a greater average thickness of metal removed.

The data for the time comparison provided several visible trends. The three by seven minute testing was more effective at etching both heated and non-heated Ti-6-4 pieces after the first two baths when the Ti concentration in each was 0 g/L. After the initial bath pieces, both bath time frames proved to be relatively equal in terms of weight removal per surface area. An interesting trend of both Ti-6-4 graphs was that at the end when the bath concentration of Ti was at its highest, the amount of metal removed for four by five minute testing was higher than that removed by the three by seven minute testing. This is possibly due to the added rinse in between dips removing excess titanium that has built up on the surface of the pieces, such that the reaction with the acid can proceed as expected. In the case of the non-heated TI-6-4 ELI pieces, the four by five minute testing proved to be more effective at etching, while in the heated pieces both time frames seemed equally effective at removing alpha case.

Comparing metal type, Ti-6-4 and Ti-6-4 ELI for four by five minute testing, the heated and non heated TI-6-4 ELI pieces had a higher metal removal than their Ti-6-4 counterpart. On the contrary, the Ti-6-4 pieces for the three by seven minute testing had a higher metal removal. This average included all data regardless of inconsistencies. The averages and standard deviation is summarized in Table 2.

Table 2: Average Weight per Surface Area Removed

	4x5 Minute (g/in^2)	Deviation	3x7 Minute (g/in^2)	Deviation
Ti-6-4	0.375	0.130	0.484	0.438
Ti-6-4 ELI	0.426	0.051	0.303	0.074
Ti-6-4 Heated	0.265	0.212	0.28	0.127
Ti-6-4 ELI Heated	0.283	0.138	0.238	0.067

The heated Ti-6-4 and TI-6-4 ELI pieces went through a similar heating procedure as an average manufactured titanium part and were placed in a furnace at 1700°F for four hours. Comparing how the alpha case etches opposed to non-heated titanium was an attempt to provide Wyman-Gordon with a more accurate time for which pieces can be dipped without removing excess titanium while removing alpha case. Figures in Appendix A show the metal removal of heated pieces against non-heated pieces for four different scenarios consisting of two different dipping procedures for each of the two alloys, Ti-6-4 and Ti-6-4 ELI.

The most apparent observation is the general trend that the non-heated pieces seem to have experienced greater metal removal in all situations. This could be due to a few different possibilities. One of which may make the most sense is that there is no alpha case on these test pieces. The rate of the chemical reaction which takes place due to the acid may favor non-heated titanium over the oxidized and restructured alpha case form of titanium. Another potential reason for this difference could be based on the temperature at which the reaction took place.

The acid beakers were placed in an ice bath. After the first few dips the ice would melt and the acid beaker would settle into the mixture more rather than sitting on top of the ice. The non-heated test pieces were dipped first before the heated alpha case pieces, and thus the alpha case pieces may have experience a slightly lower temperature which reduces the rate of reaction. Another observation is that the non-heated test pieces seem to be much more volatile in terms of metal removed. The heated pieces follow a much more consistent trend with much fewer drastic changes. This may be explained again by the fact that the alpha case may react differently in HF acid than non-heated titanium. Slight conditional changes such as temperature, acid concentration, and titanium concentration may have a greater effect on the metal removal of the non-heated titanium alloy pieces. The different structure of the alpha case may be the reason for why these changes have less drastic effects and results on the heated pieces.

Acid Concentration Relationships

Metal removal is dependent on a particular balance between acid concentration and titanium concentration in the bath. The graph below shows the concentration of hydrofluoric acid and corresponding amount of metal removed of the heated pieces for every bath day. The amount of metal removed is multiplied by a factor of twenty so it is easier to see the general trend on a smaller range on the axis. The amount of metal removed is clearly dependent on the hydrofluoric acid concentration. Removal for both three by seven minute tests and four by five minute tests follow the rise and fall of the acid concentration day by day.

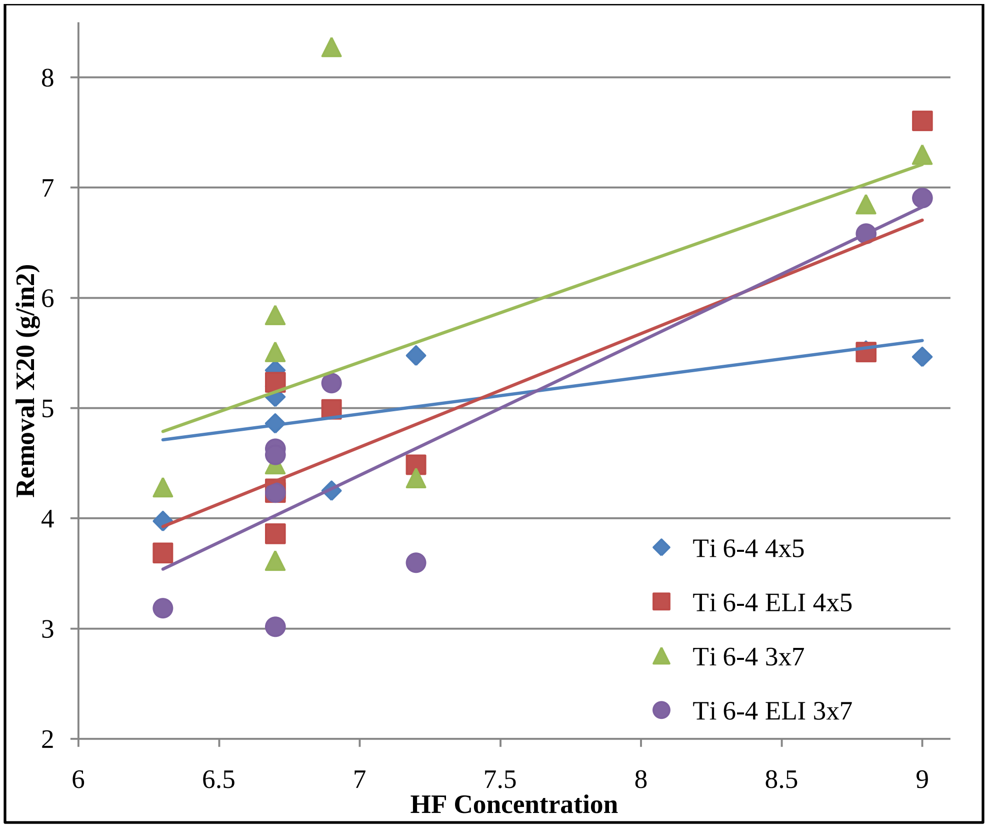

Figure 6: Metal Removal Dependence on HF Concentration

The R^2 values in Table 3, also known as correlation coefficients, for the Ti-6-4 ELI experiments are much higher than Ti-6-4. This means that the TI-6-4 ELI experiments were more cohesive and closely followed the linear regression. The Ti-6-4 experiments (four by five minute and three by seven minute) had a much lower value, meaning the data had high deviation from one point to another. It would be beneficial to repeat the Ti-6-4 experiments to see if the results will better fit the linear trend, similar to the Ti-6-4 ELI experiments.

Table 3: R^2 Values

Type	Slope	R^2
Ti-6-4 4x5	0.332	0.339
Ti-6-4 3x7	0.897	0.308
Ti-6-4 ELI 4x5	1.029	0.716
Ti-6-4 ELI 3x7	1.216	0.747

The nitric acid is a weaker acid than hydrofluoric acid therefore the metal removal is not as strongly dependent on that concentration. As the hydrofluoric acid concentration decreases with use, the amount of titanium removed decreases as well. The bath is periodically spiked with hydrofluoric and nitric acid to prolong the bath life and save money. In the table below, it can be seen that the bath was spiked on days seven, nine and possibly four. Day four is missing because the tank was used on a Saturday and the usual titration tests were not completed in the lab.

Table 4: Acid Bath Daily Titrations

Bath Day	%HF	%HNO3	Ti (g/L)	HF Added	HNO3Added
1	9	10	0		75
2	8.8	9.4	0		
3	6.9	9.2	7	175	50
4	N/A	N/A	N/A		
5	6.7	9.4	14		
6	6.7	8.7	21	150	
7	7.2	7.8	23	250	180
8	6.3	7.8	30	150	100
9	6.7	8.5	35	150	150
10	6.7	7.6	35		

The bath is tested every day to monitor the acid concentrations and titanium levels. As the titanium concentration increases in the bath, the driving force for dissolution decreases. For this reason, the bath is refreshed when the titanium concentration reaches 40 g/L. As of right now, there is no economical method for removing the titanium from the bath so Wyman-Gordon opts to start over with a fresh bath. A fresh bath is 9% hydrofluoric acid, 10% nitric acid by volume and 0 g/L of titanium. The acid spikes prolong the bath life and keep etch rates at an optimum level but the titanium concentration is the main constraint. The figure below does not show a clear relationship between titanium concentration and the experimental metal removal of all four conditions, but this may be due to the lack of agitation or other experimental error. It is known in the chemical milling industry that the titanium concentration is a direct factor in the efficiency of metal removal.

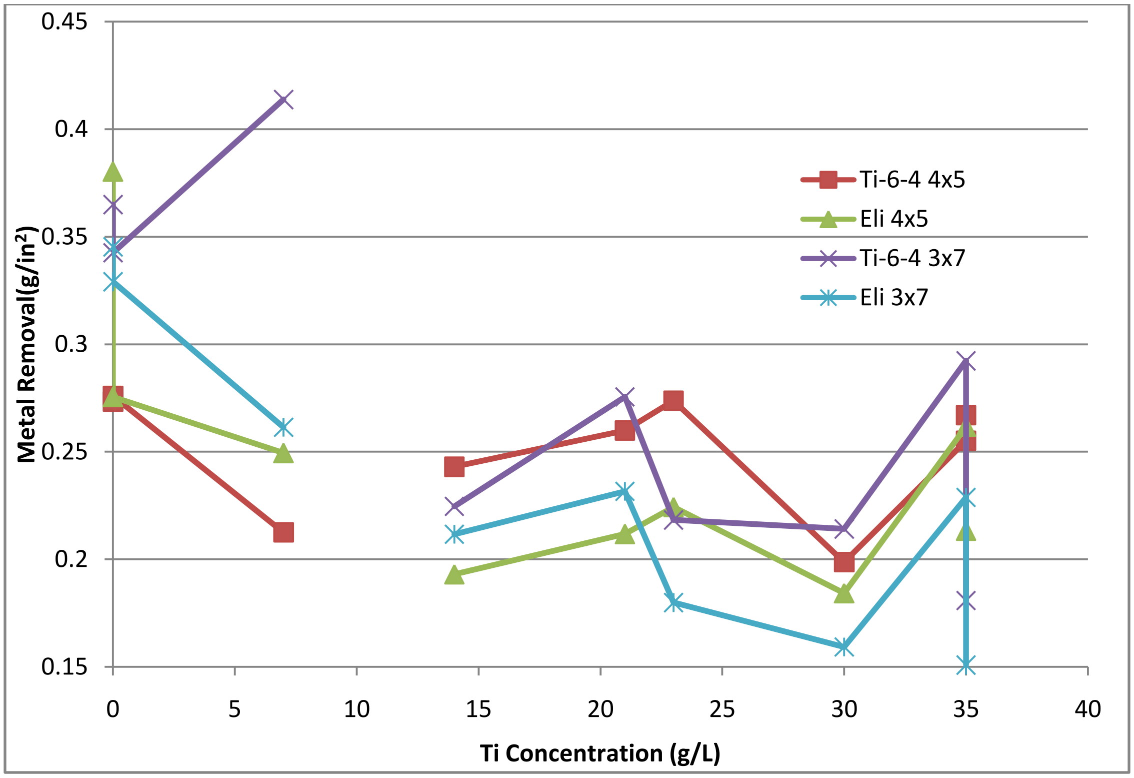

Figure 7: Metal Removal Dependence on Ti Concentration

Optimum Bath Life

There are two main components of bath life: acid concentration and titanium concentration. When the titanium concentration reaches approximately 40g/L, but does not exceed 50g/L, the bath gets dumped. This is because the amount of metal removed decreases as the titanium concentration increases. If alpha case remains on the part, failure is a possibility and the customer must machine the part to their specifications.

To compensate for this, the bath gets spiked with fresh acid. When there is 10% HNO_3, there is a limit between 8.5 and 11% HNO_3. Similarly, when there is 8% HF, there is a limit between 7 and 9% HF. Typically, the limit lies to the lower end. The chart, shown below, specifies the necessary amount of acid to return the bath to normal specifications. The 8% HF chart numbers are multiplied by 1.5 because Wyman-Gordon previously used 70% HF rather than the 49% solution they now use.

Microscopy

As shown by the images below, when heated at 1700°F for 4 hours, TI-6-4 ELI pieces showed an alpha case thickness of 38.65 micrometers (0.001521 inches) and Ti-6-4 pieces showed a thickness of 42.03 micrometers (0.001655 inches). It was an assumption that the alpha case thickness formed on each test piece was uniform. Ultimately the goal of this experimentation was to remove the alpha case; however, this data combined with the feeler gauge data reveals that that did not happen (Titanium Alpha Case Prevention, 2010).

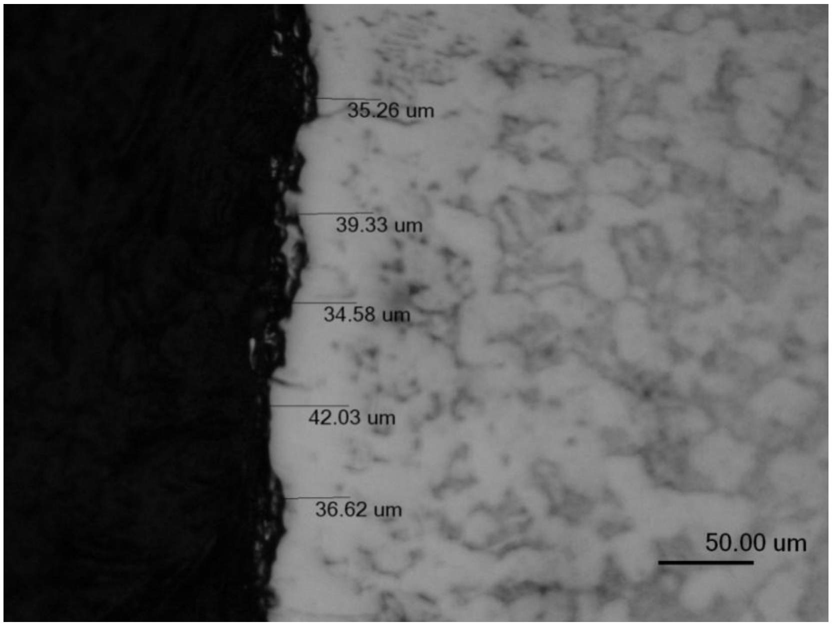

Figure 8: Microscopy Photo of Ti-6-4 (Titanium Alpha Case Prevention)

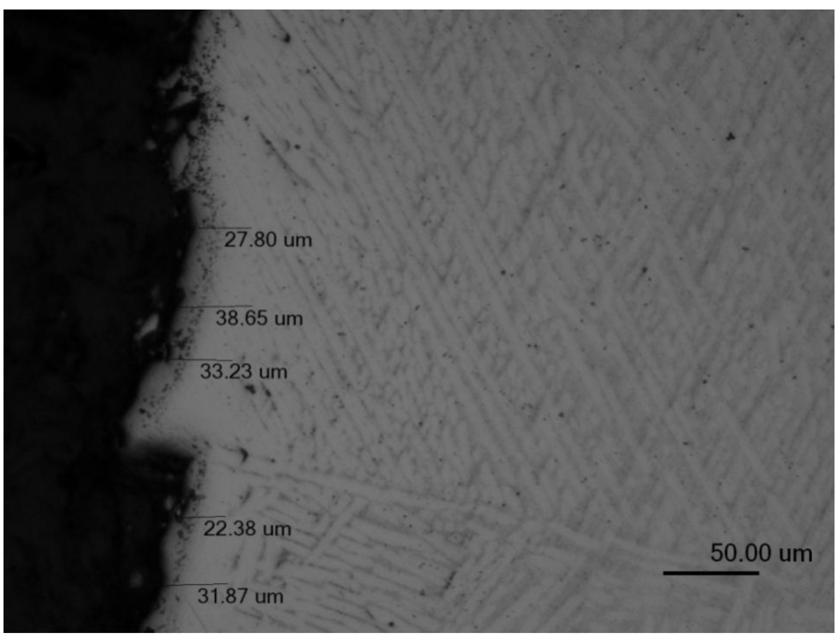

Figure 9: Microscopy Photo of Ti-6-4 ELI (Titanium Alpha Case Prevention)

The thickness of alpha case formed on titanium during the heating process is dependent on the oxygen concentration, temperature, and amount of time which the piece is heated for. The size of the piece therefore should have no effect on the developed thickness, which makes the thickness found on small experimental pieces comparable to that of production size pieces. The typical heating conditions used at Wyman-Gordon leads to an approximate thickness of 0.0015 inches of alpha case. This is one tenth of the 0.015 inches that Wyman-Gordon removes via chemical milling. Therefore, Wyman-Gordon is removing more alpha case than necessary. This is worthwhile as a safeguard to not removing all the alpha case, however, may be more than is needed to still be certain that the entire thickness of alpha case is removed. By removing less thickness, bath life could be increased in turn saving money spent on spend on expensive acids.

Chapter Five: Conclusion and Recommendations

Upon completion of all experimentation, it was determined that the initial experimental setup was flawed and did not yield all too conclusive data. To ensure the effectiveness of future projects, the following changes are suggested: ensure uniformity among test pieces (size and shape), suspend the pieces in the acid bath while they are being etched, select and monitor a constant temperature, and finally agitate experimental baths to more closely mimic Wyman-Gordon's current process. Another option for experimentation is to test both a heated and non-heated titanium piece in the bath simultaneously, as to avoid variables of acid and titanium concentration and temperature. A newly conceived experimental procedure has been attached in Appendix C.

Feeler gauge analysis proved to be an inaccurate measurement of metal removed since the faces of test pieces were not etched uniformly, and thus results were based off a measurement of weight removed per exposed surface area. It is recommended, because of the inaccuracies and probability of human error associated with the use of a feeler gauge, that Wyman-Gordon consider the use of weight removed per surface area as a new measurement for metal removal. However to proceed with this method, a standard for kg/m^2 removed would have to be set that is currently equivalent to Wyman-Gordon's current standard of removing a thickness of 0.015 inches. More research will have to be done into alpha case density to make this a plausible method of measuring metal removal.

Although it was a goal of this project, little information was gathered regarding etch rates. To gain a better understanding of the speed at which metal is removed, Wyman-Gordon will have to conduct more fine tuned and detailed experimentation. This would require the measurement of metal removed between dips to also understand the changes in those rates in regards to Ti concentration. However, a clear conclusion from this experimentation is that Ti-6-4 and TI-6-4 ELI pieces do not etch at the same rate, and Ti-6-4 pieces do not etch at the same rate as their heated counterparts.

TI-6-4 ELI pieces had a higher average amount of metal removed in four by five minute tests; however, regular Ti-6-4 pieces had a greater average metal removal in three by seven minute testing. An interesting trend of the Ti-6-4 pieces was an increased removal for four by five minute testing in later baths. Although only a slight upward trend in later baths, more and shorter dips in later baths could prolong bath life and save time before dumping. Heated pieces averaged about 50-80% as much metal removed on average as their non-heated counterpart. It is recommended that more research be done into the resulting thickness of alpha case on forged parts, because removing excess thickness from a part will not only result in alpha case removal but more than necessary titanium removal.

Titanium and hydrofluoric acid concentrations within the acid tanks are suspected to play a key role in the chemical milling process. There is a direction correlation between HF concentration within the bath and the amount of metal removed. However, when etch rate is compared with the titanium concentration within the bath, the data does not prove a clear relationship between the two. As the bath life increased, more acid had to be added to maintain the proper concentrations. It is recommended that more research be done with regards to titanium concentration versus metal removal as the two should have an inverse relationship.

Finally, spiking the acid baths with nitric and hydrofluoric acid is a necessary measure in order to prolong the life of the bath. Although this is an accepted and effective method of prolonging bath life, it is not one that eliminates the issue of dumping waste acid. More research should be done into alternative techniques to prolong acid bath life including but not limited to: using a chemical reaction to precipitate excess titanium out of the bath, distilling waste acid to separate titanium from pure nitric and hydrofluoric acid, and filtering waste acid of titanium.

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Appendix A: Graphs and Data

Time Comparison

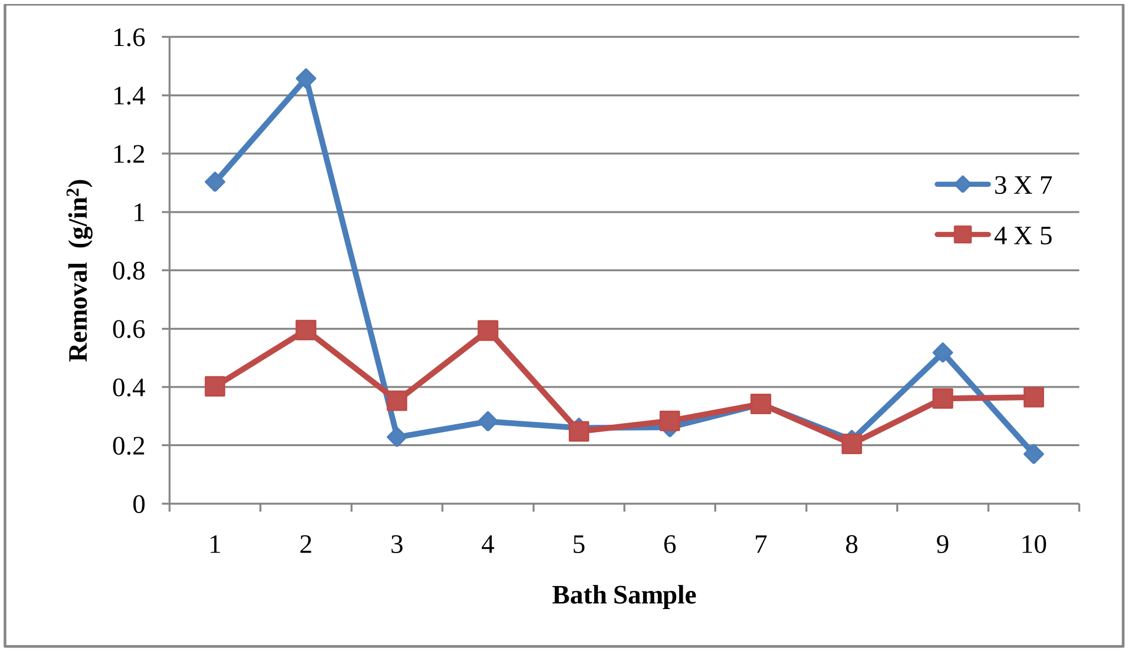


Figure 10: Weight Loss of Ti-6-4 at Two Dip Times

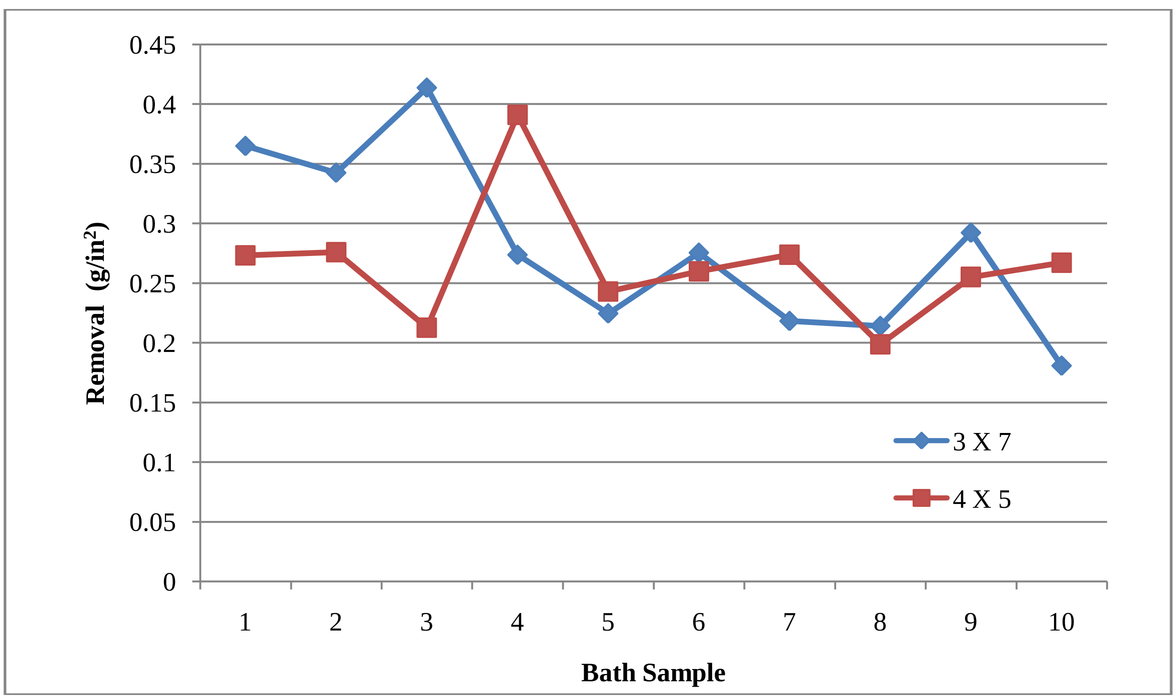


Figure 11: Weight Loss of Ti-6-4 Heated at Two Dip Times

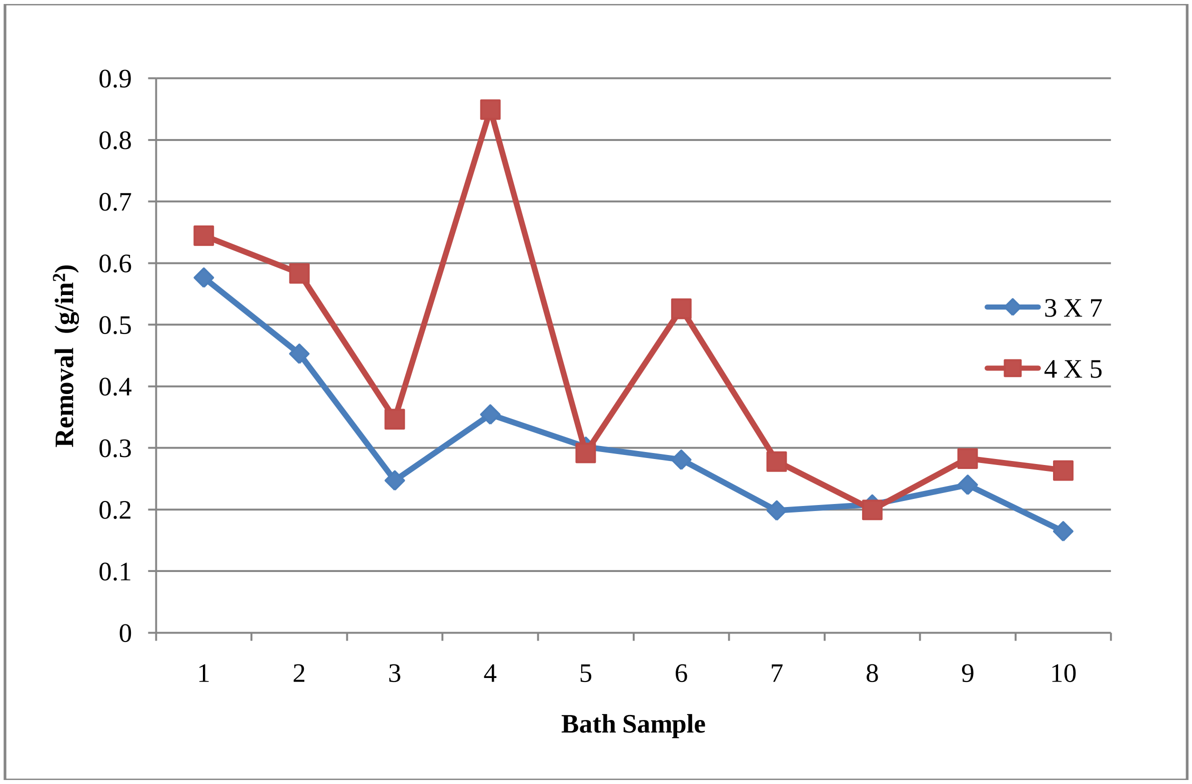


Figure 12: Weight Loss of Ti-6-4 ELI at Two Dip Times

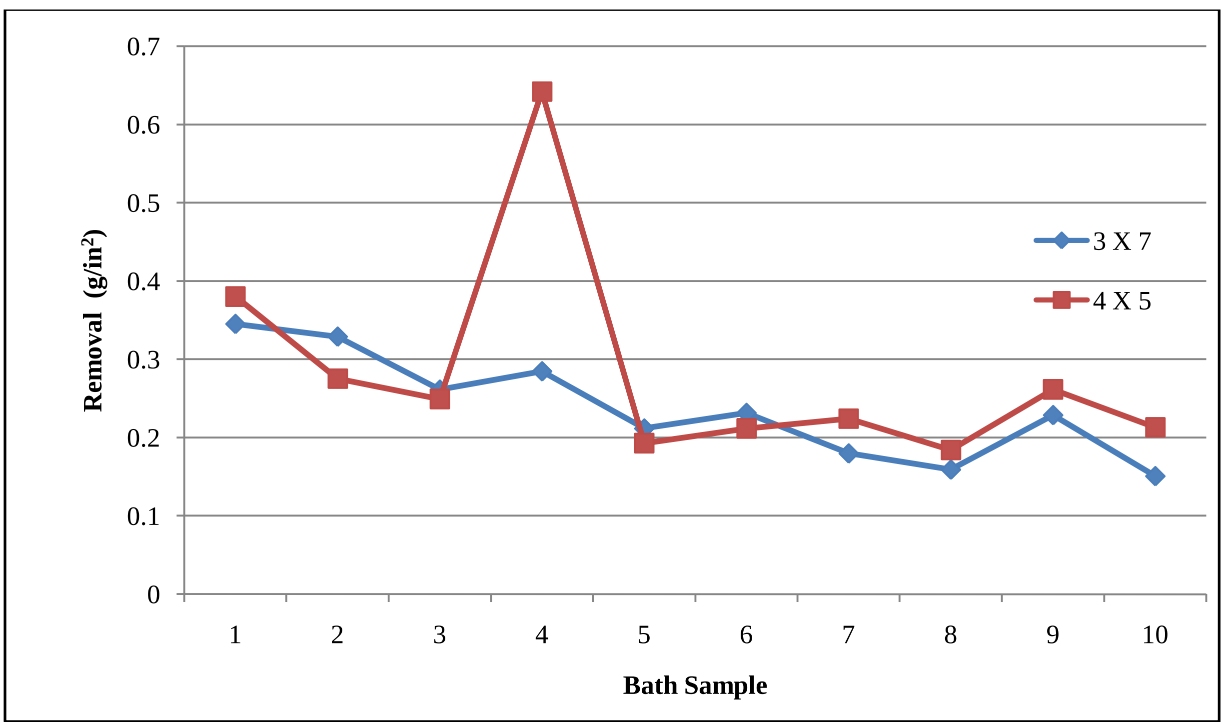


Figure 13: Weight Loss of Ti-6-4 ELI at Two Dip Times

Feeler Gauge

Figure 14: Feeler Gauge Measurements of Ti-6-4 Heated, Three by Seven Minutes

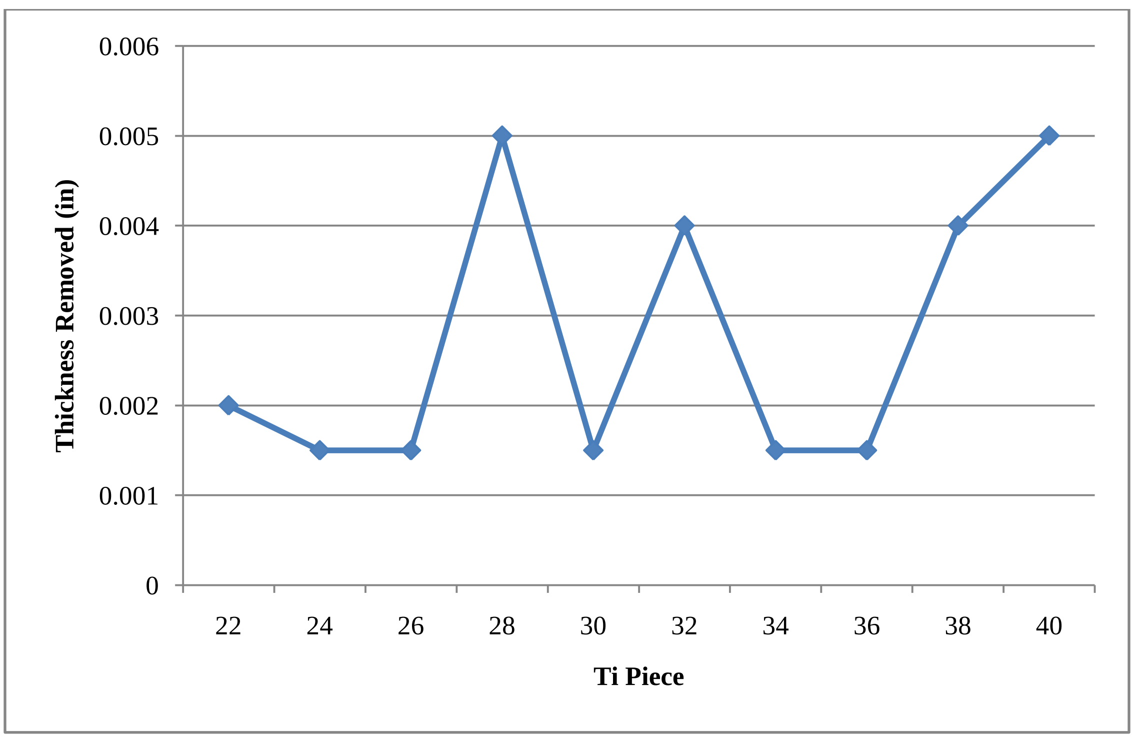


Figure 15: Feeler Gauge Measurements of Ti-6-4 Heated, Four by Five Minutes

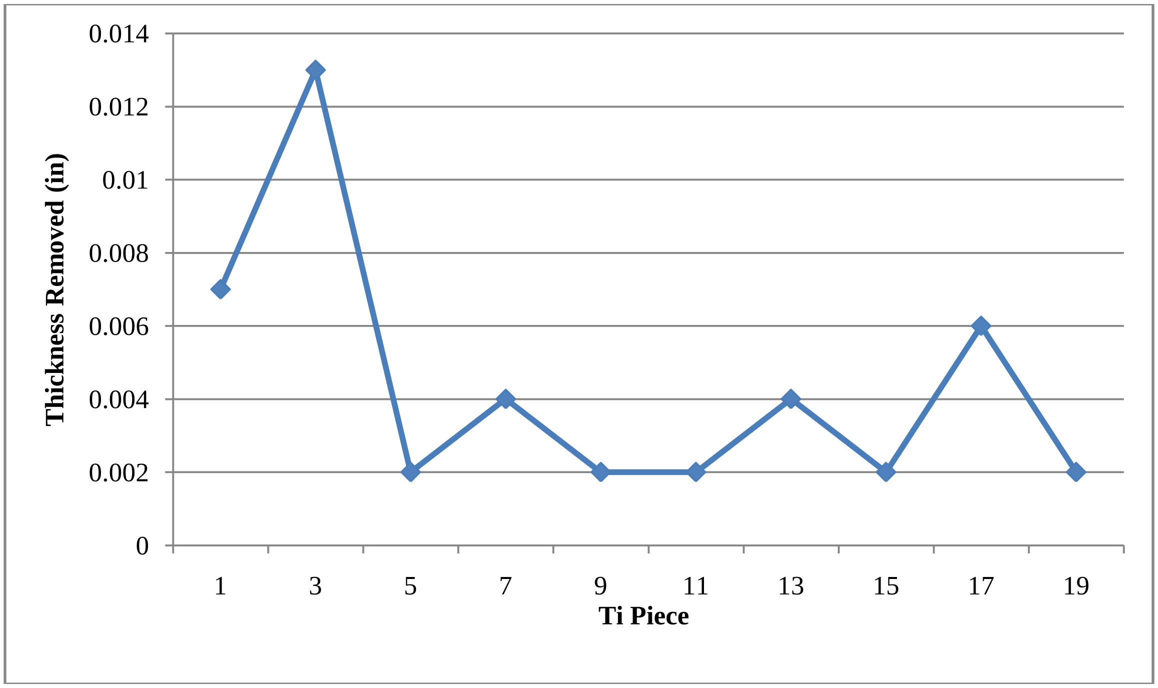


Figure 16: Feeler Gauge Measurements of Ti-6-4, Three by Seven Minutes

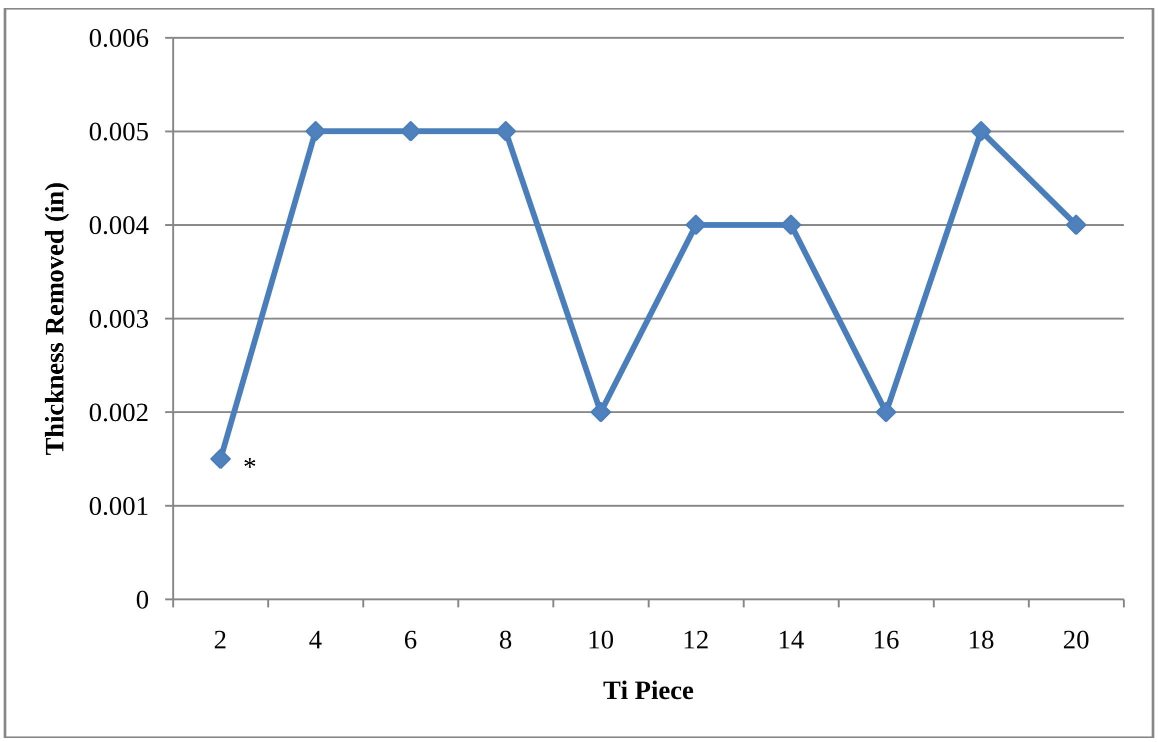


Figure 17: Feeler Gauge Measurements of Ti-6-4, Four By Five Minutes

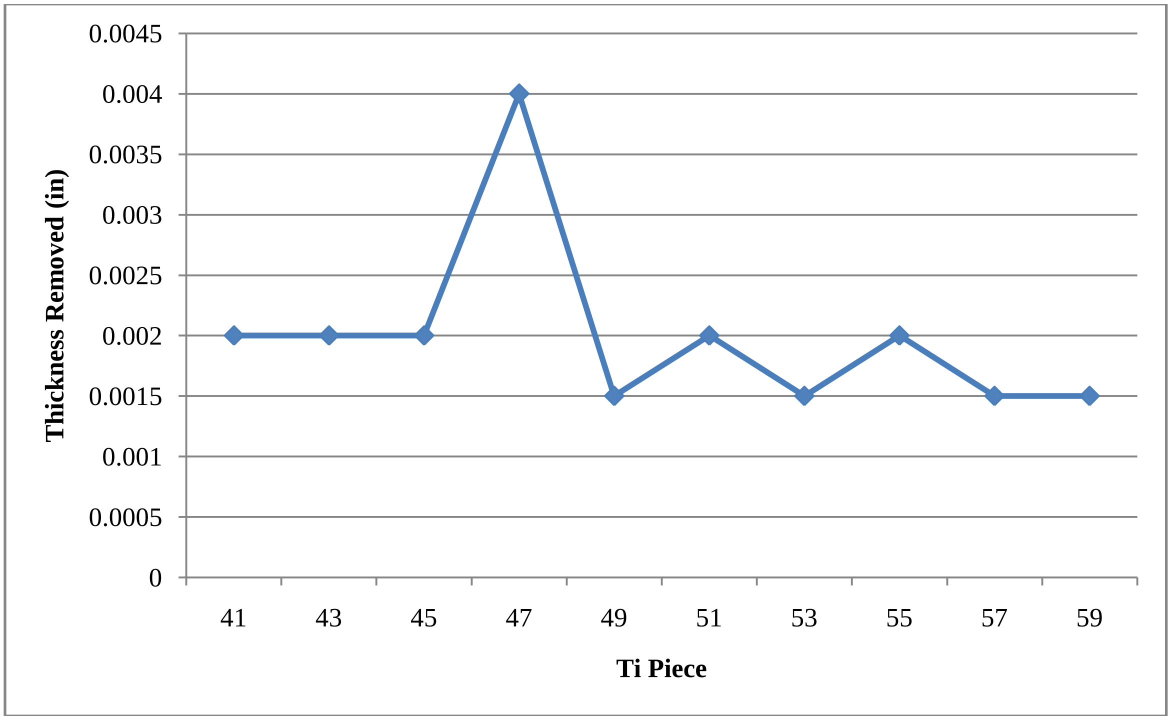


Figure 18: Feeler Gauge Measurements of Ti-6-4 ELI Heated, Three by Seven Minutes

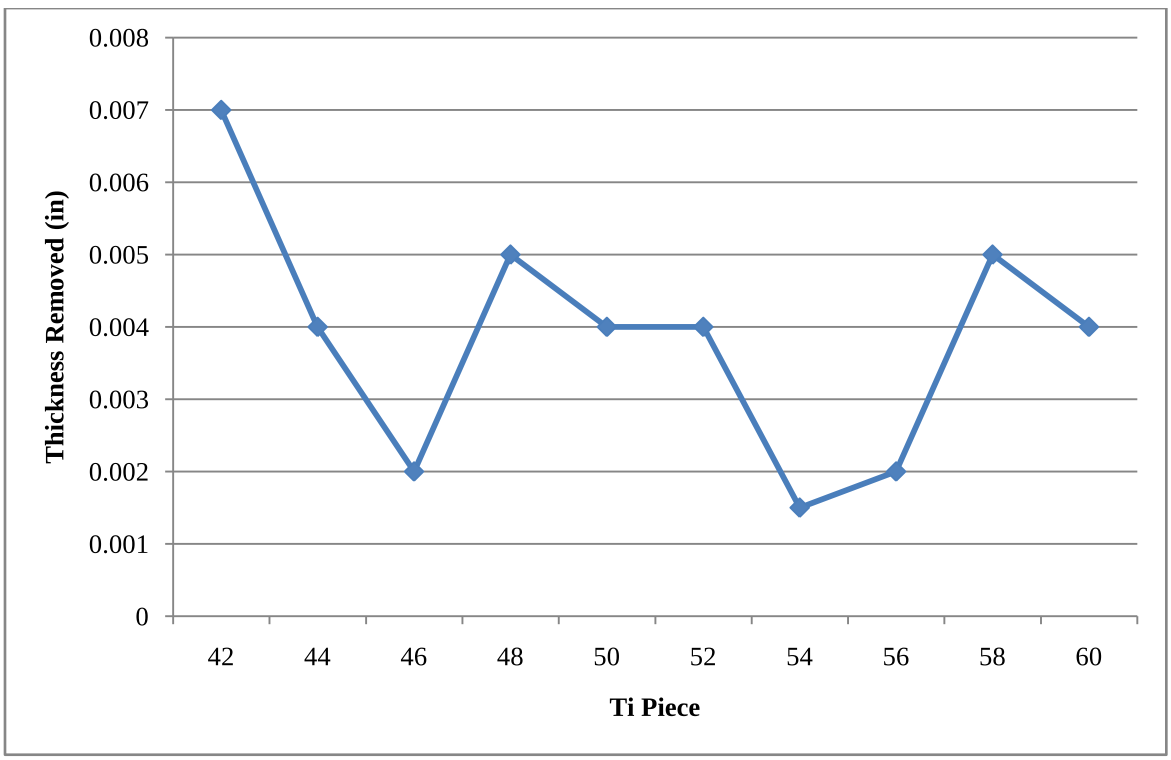


Figure 19: Feeler Gauge Measurements of Ti-6-4 ELI Heated, Four By Five Minutes

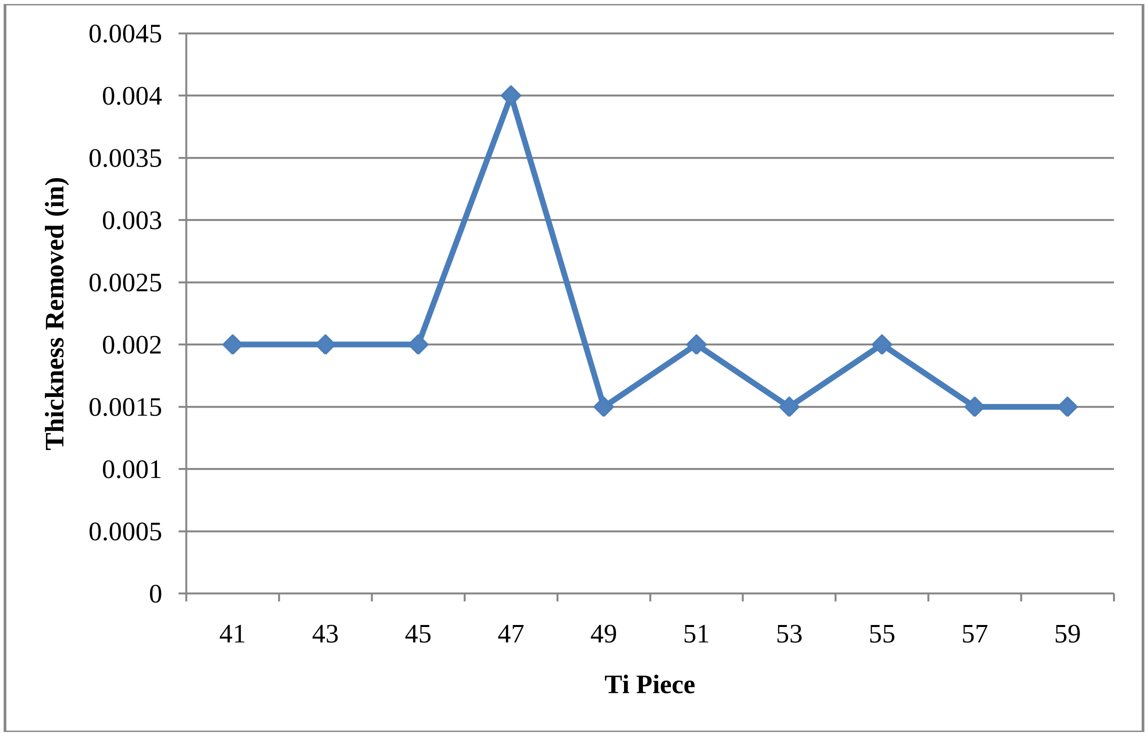


Figure 20: Feeler Gauge Measurements of Ti-6-4 ELI, Three By Seven Minutes

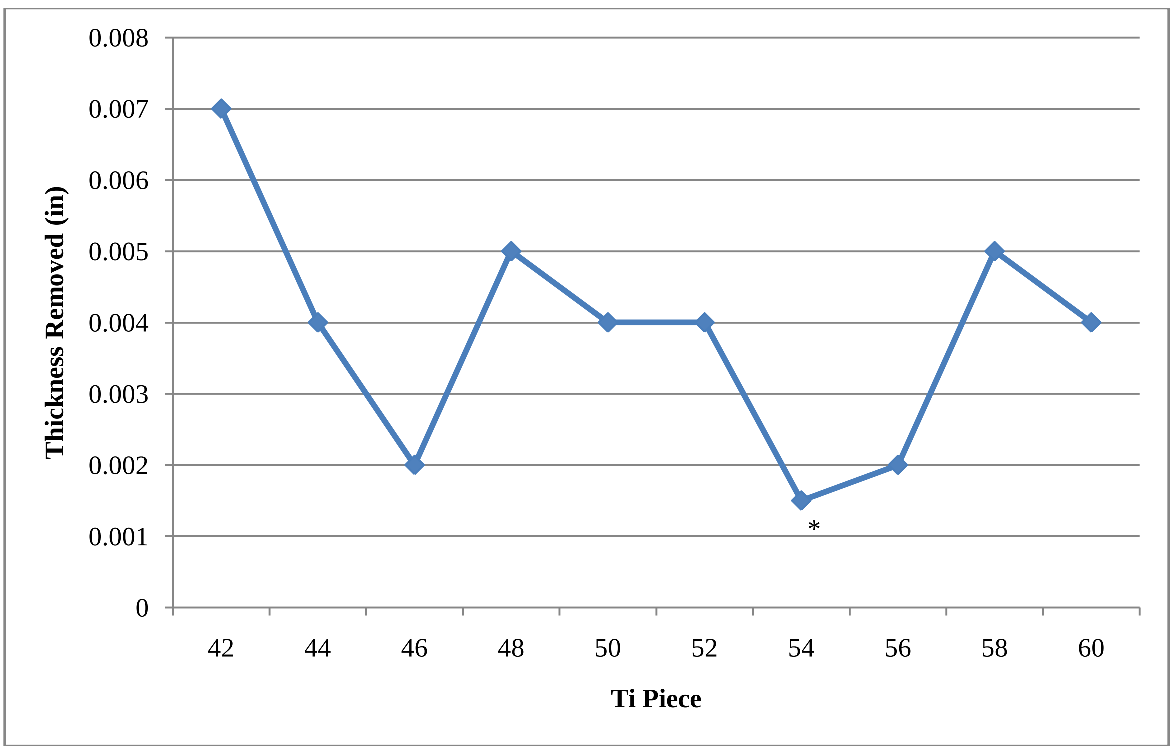


Figure 21: Feeler Gauge Measurements of Ti-6-4 ELI, Four By Five Minutes

Metal Types

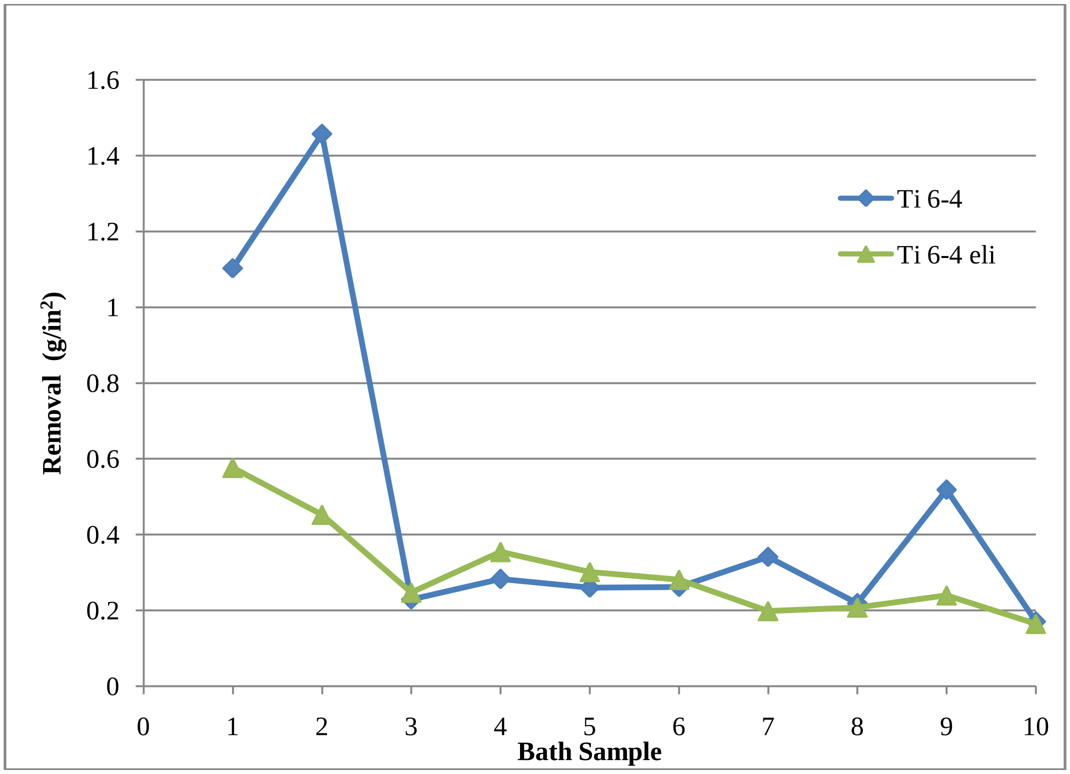


Figure 22: Non-Heated Ti Pieces Dipped Three by Seven Minutes

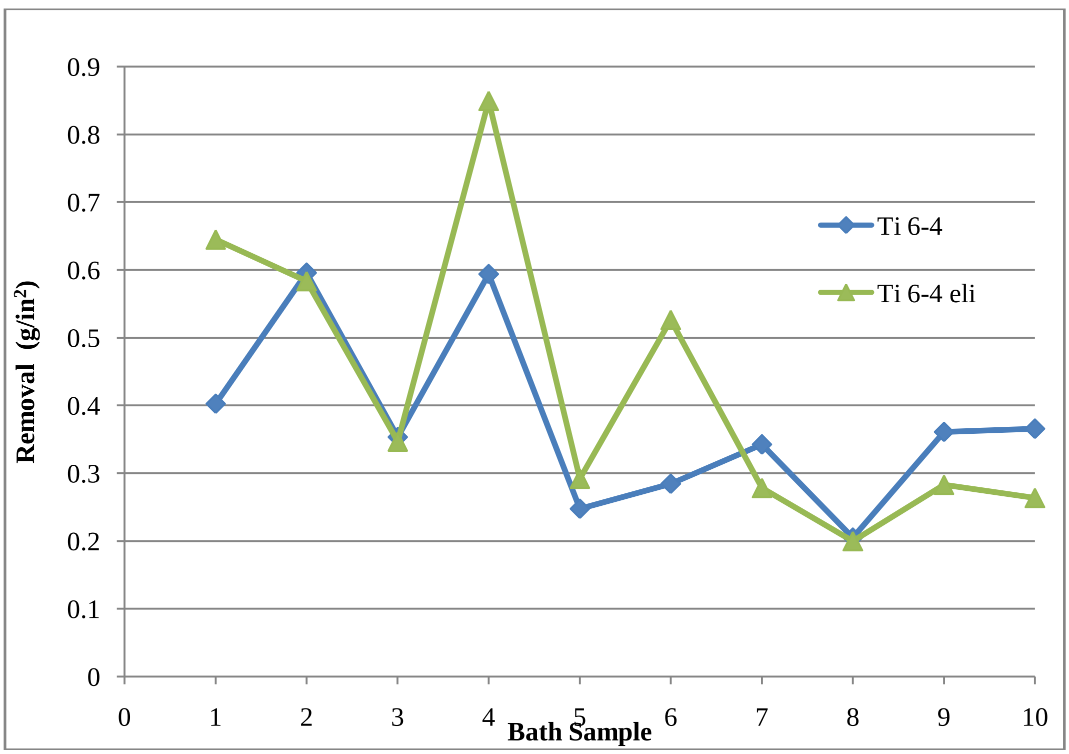


Figure 23: Non-Heated Ti Pieces Dipped Four by Five Minutes

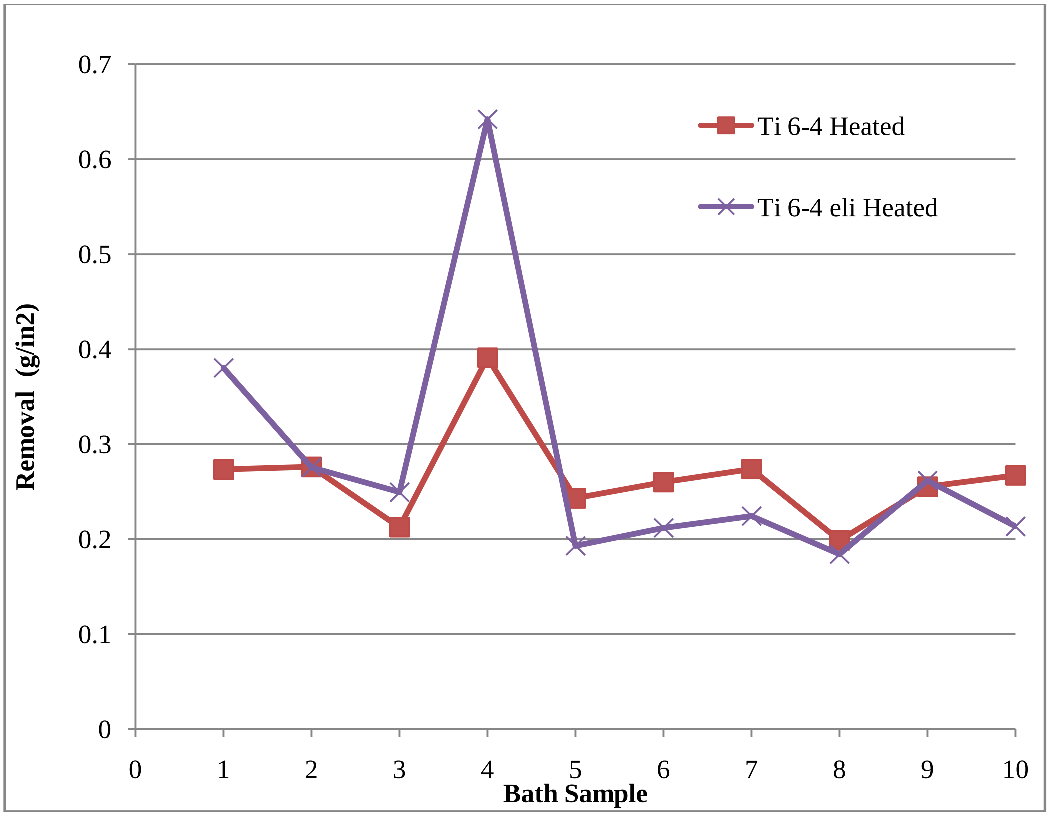


Figure 24: Heated Ti Pieces Dipped Four by Five Minutes

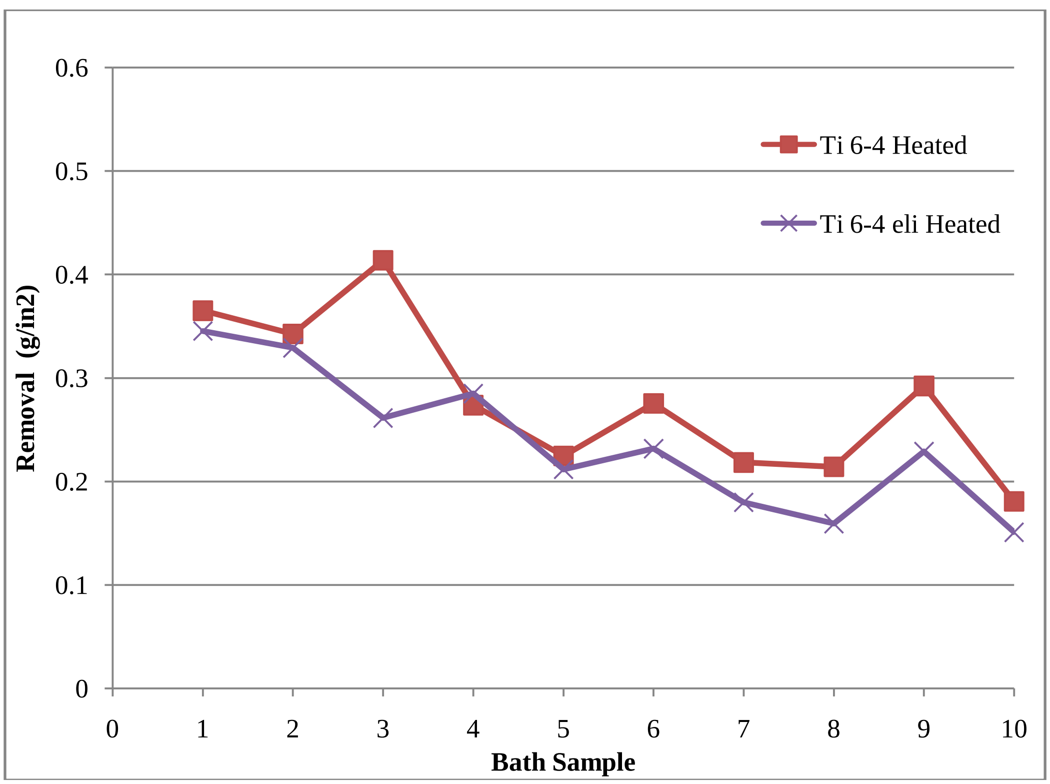


Figure 25: Heated Ti Pieces Dipped Three by Seven Minutes

Heated versus Non-Heated

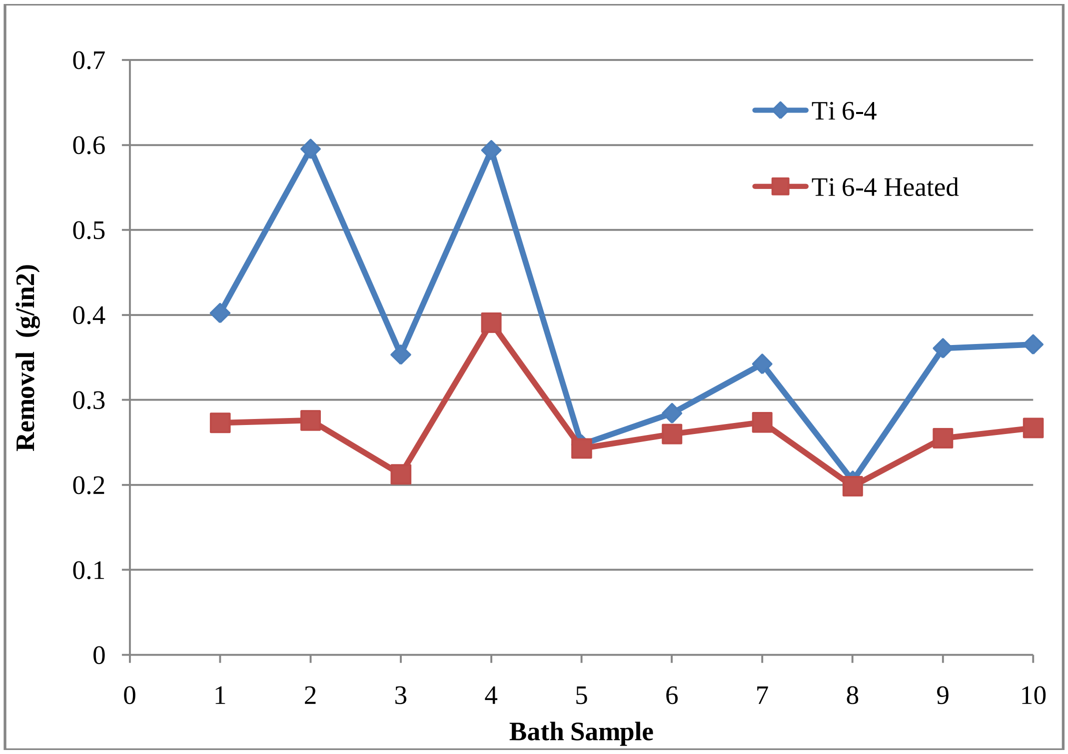


Figure 26: Heated and Non-Heated Ti Pieces Dipped Four by Five Minutes

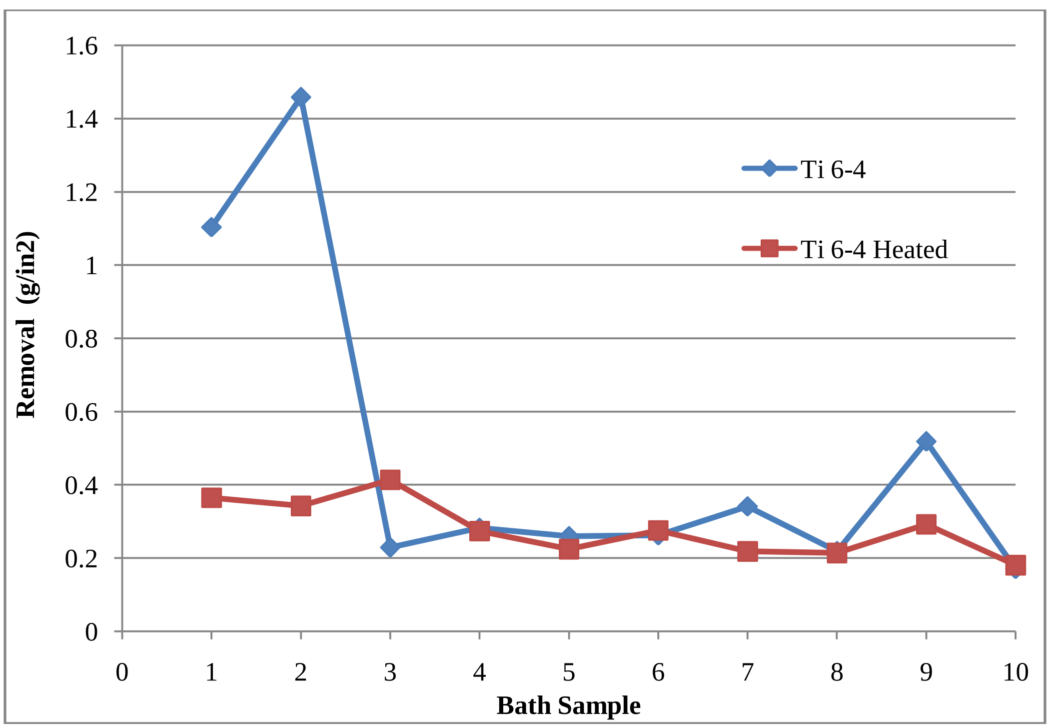


Figure 27: Heated and Non-Heated Ti Pieces Dipped Three by Seven Minutes

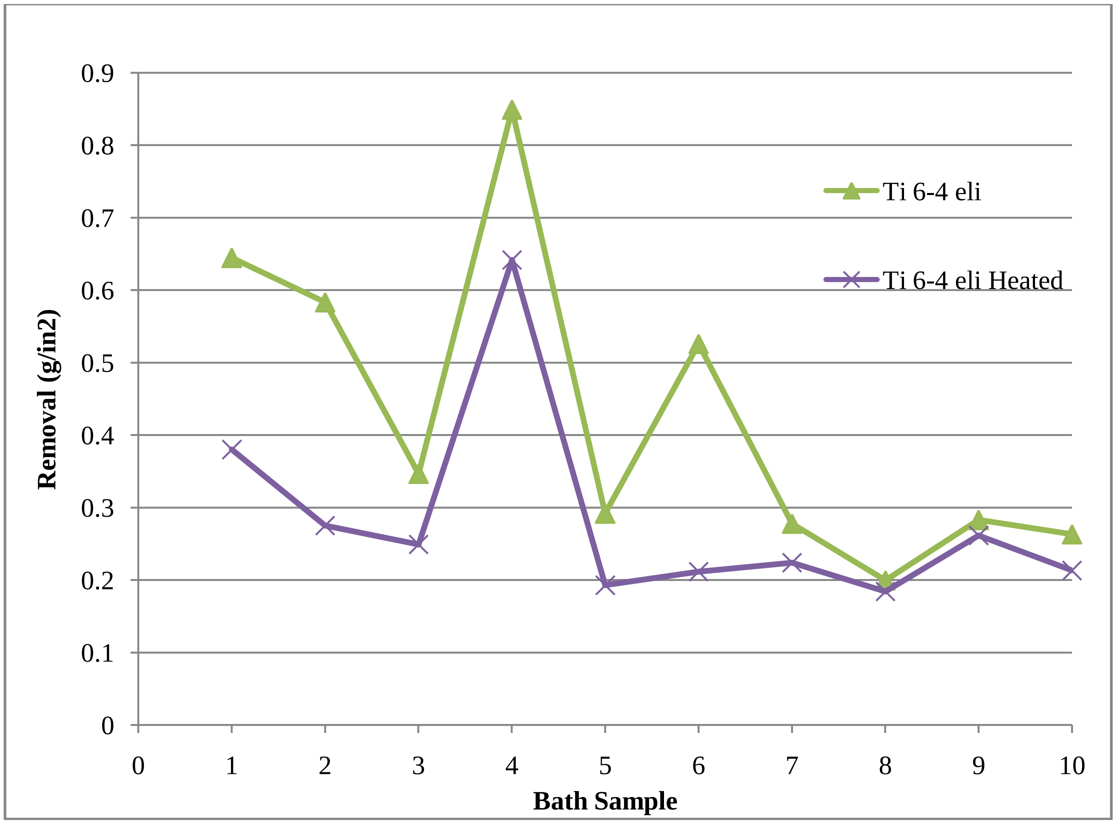


Figure 28: Heated and Non-Heated ELI Pieces Dipped Four by Five Minutes

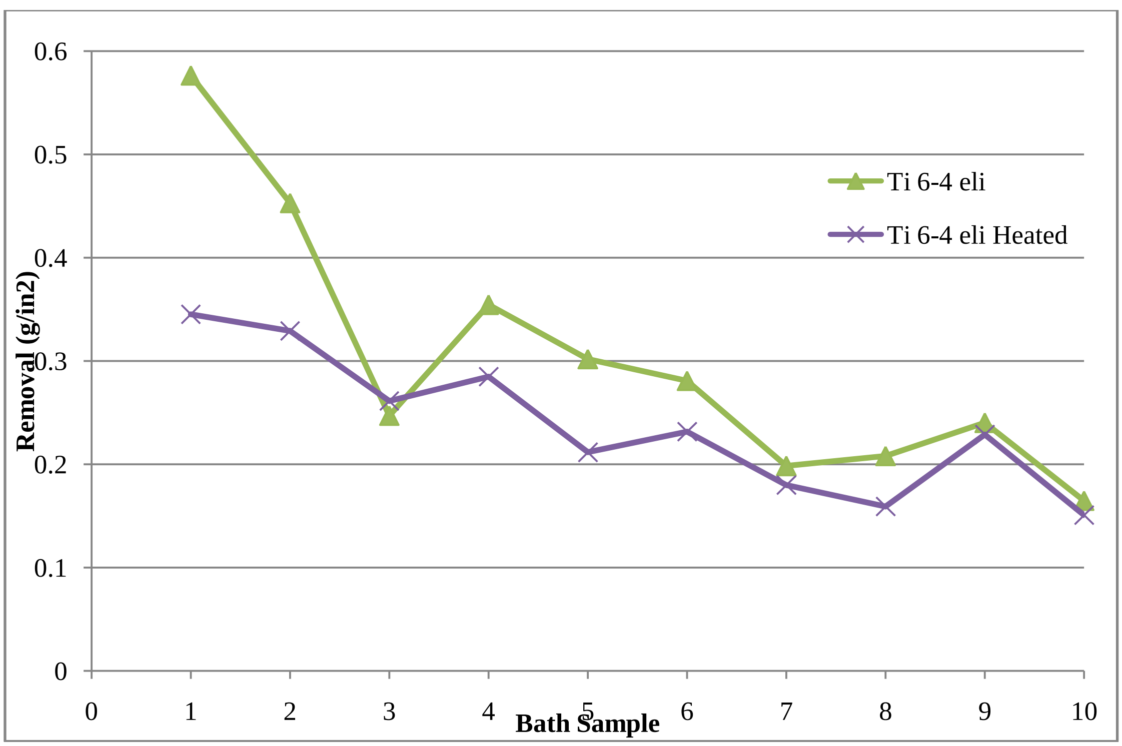


Figure 29: Heated and Non-Heated ELI Pieces Dipped Four by Three by Seven Minutes

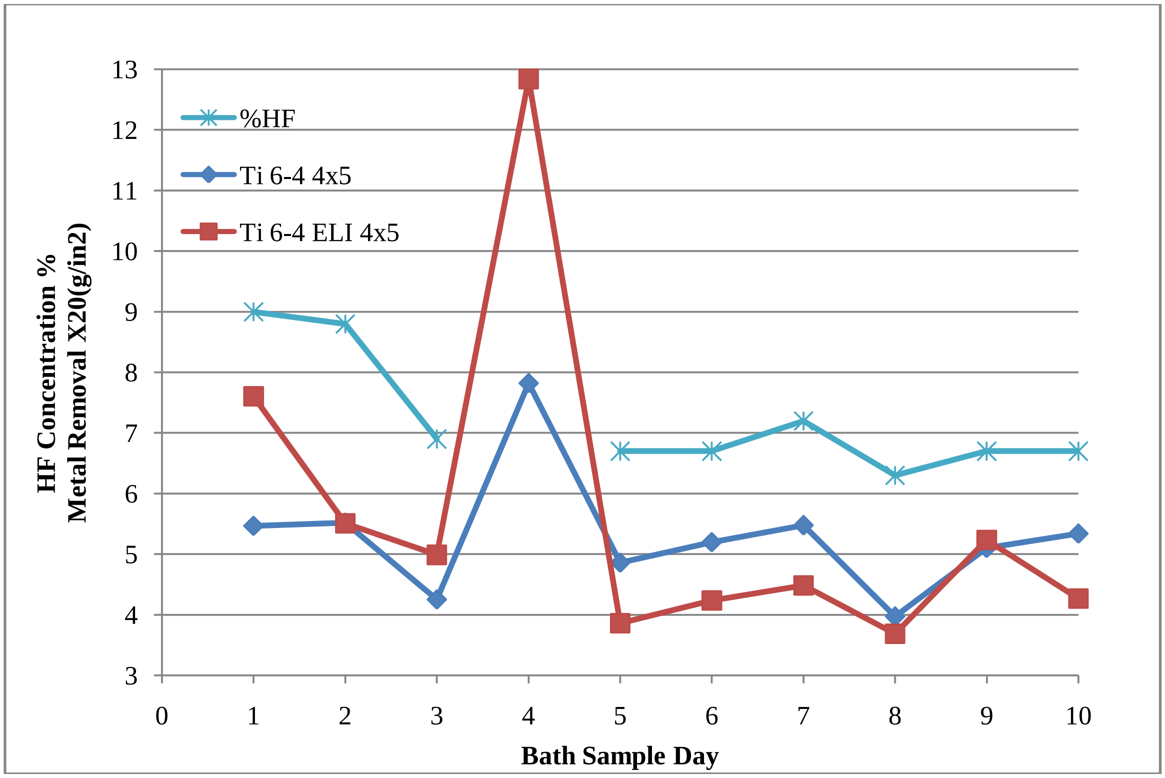


Figure 30: Metal Removal Dependence of HF Concentration for Four by Five Minute Dips

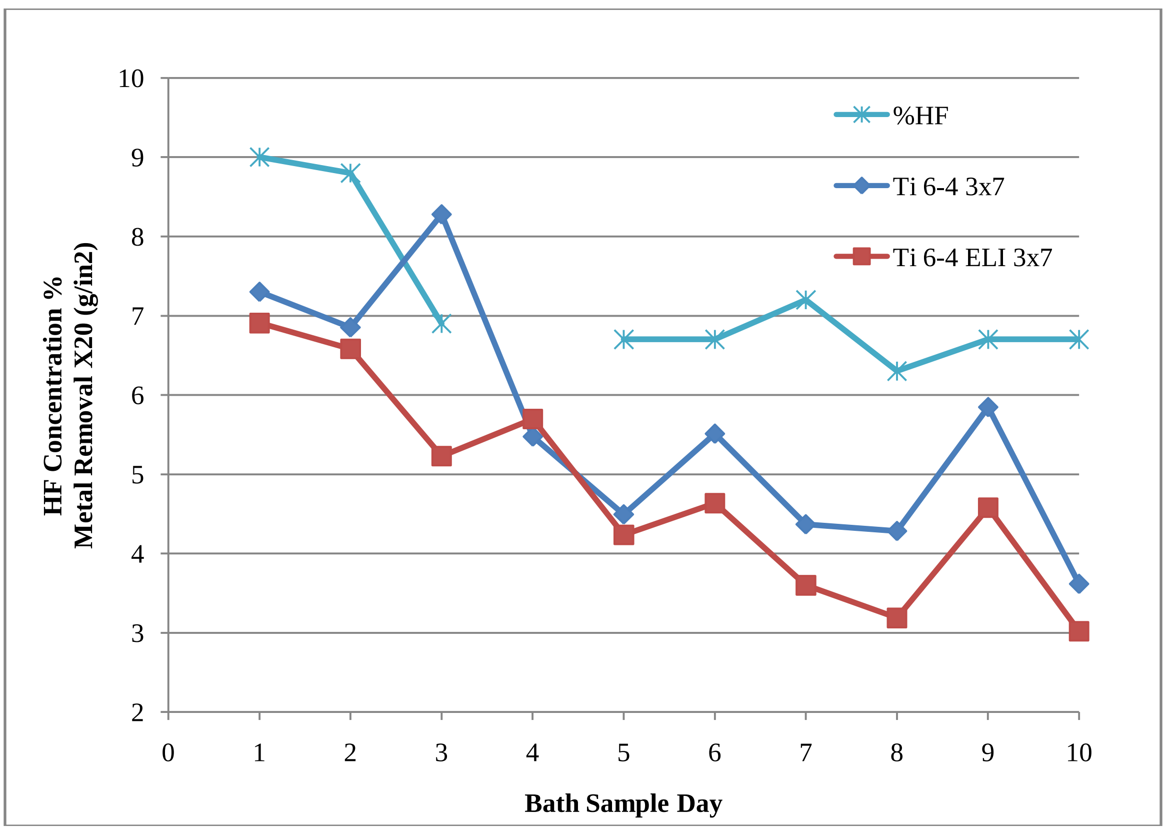


Figure 31: Metal Removal Dependence of HF Concentration for Three by Seven Minute Dips

Table 5: Data of Three by Seven Minute Dips

Test Coupon Number	Metal Type	Bath Sample Used	Initial Weight (g)	Weight after Heating/Blasting (g)	Surface Area (in^2)	Weight after Chemical Milling (g)	Weight Removal (g/in^2)
1	Ti-6-4	1	76.015	N/A	3.593	72.051	1.103
3	Ti-6-4	2	86.483	N/A	4.191	80.373	1.457
5	Ti-6-4	3	84.856	N/A	4.382	83.853	0.228
7	Ti-6-4	4	84.595	N/A	4.156	83.420	0.282
9	Ti-6-4	5	86.696	N/A	4.499	85.525	0.260
11	Ti-6-4	6	85.458	N/A	4.483	84.282	0.262
13	Ti-6-4	7	84.747	N/A	4.531	83.201	0.341
15	Ti-6-4	8	82.179	N/A	4.512	81.193	0.218
17	Ti-6-4	9	89.528	N/A	5.034	86.919	0.518
19	Ti-6-4	10	82.201	N/A	4.736	81.394	0.170
21	Ti-6-4Heated	1	73.175	72.609	3.406	71.365	0.365
23	Ti-6-4Heated	2	83.002	82.317	4.062	80.925	0.342
25	Ti-6-4Heated	3	84.819	84.985	4.124	83.278	0.413
27	Ti-6-4Heated	4	89.579	88.75	4.286	87.576	0.273
29	Ti-6-4Heated	5	83.043	82.344	4.317	81.374	0.224
31	Ti-6-4Heated	6	81.265	80.677	4.229	79.511	0.275
33	Ti-6-4Heated	7	85.702	85.015	4.605	84.009	0.218
35	Ti-6-4Heated	8	84.499	83.793	4.709	82.784	0.214
37	Ti-6-4Heated	9	87.336	86.614	4.911	85.178	0.292
39	Ti-6-4Heated	10	82.947	82.476	4.893	81.591	0.180
41	Ti-6-4 ELI	1	80.861	N/A	3.712	78.720	0.576
43	Ti-6-4 ELI	2	73.381	N/A	3.659	71.723	0.452
45	Ti-6-4 ELI	3	75.248	N/A	3.816	74.304	0.247
47	Ti-6-4 ELI	4	80.013	N/A	4.105	78.558	0.354
49	Ti-6-4 ELI	5	75.448	N/A	4.155	74.193	0.301

51	Ti-6-4 ELI	6	72.235	N/A	3.889	71.142	0.280
53	Ti-6-4 ELI	7	89.492	N/A	4.864	88.526	0.198
55	Ti-6-4 ELI	8	72.72	N/A	4.218	71.842	0.208
57	Ti-6-4 ELI	9	69.927	N/A	4.152	68.929	0.240
59	Ti-6-4 ELI	10	67.326	N/A	4.221	66.630	0.164
61	Ti-6-4 ELI Heated	1	62.011	61.325	3.082	60.260	0.345
63	Ti-6-4 ELI Heated	2	77.764	76.967	3.816	75.711	0.329
65	Ti-6-4 ELI Heated	3	78.221	77.113	3.866	76.102	0.261
67	Ti-6-4 ELI Heated	4	76.425	75.284	4.044	74.132	0.284
69	Ti-6-4 ELI Heated	5	75.841	74.794	3.983	73.950	0.211
71	Ti-6-4 ELI Heated	6	74.407	73.265	4.18	72.296	0.231
73	Ti-6-4 ELI Heated	7	73.158	72.392	4.173	71.641	0.179
75	Ti-6-4 ELI Heated	8	70.071	69.269	4.107	68.614	0.159
77	Ti-6-4 ELI Heated	9	82.401	81.36	4.766	80.269	0.228
79	Ti-6-4 ELI Heated	10	73.82	72.8	4.489	72.122	0.150

Table 6: Data of Four by Five Minute Dips

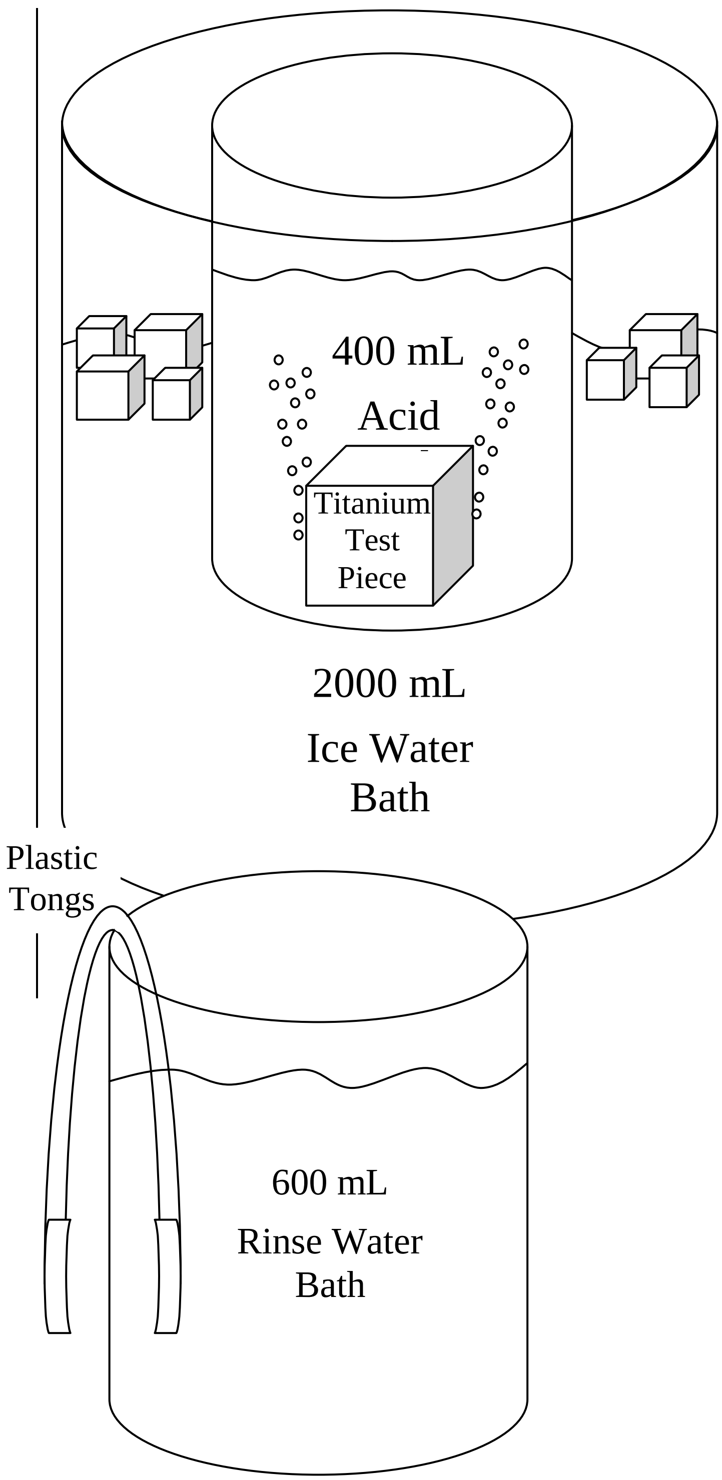
Test Coupon Number	Metal Type	Bath Sample Used	Initial Weight (g)	Weight after Heating/Blasting (g)	Surface Area (in^2)	Weight after Chemical Milling (g)	Weight Removal (g/in^2)
2	Ti-6-4	1	78.418	N/A	3.8126	76.883	0.402
4	Ti-6-4	2	85.723	N/A	4.1525	83.250	0.595
6	Ti-6-4	3	85.147	N/A	3.9307	83.758	0.353
8	Ti-6-4	4	85.058	N/A	4.383	82.454	0.593
10	Ti-6-4	5	84.821	N/A	4.77	83.640	0.247
12	Ti-6-4	6	82.21	N/A	4.574	80.909	0.284
14	Ti-6-4	7	81.604	N/A	4.3125	80.127	0.342
16	Ti-6-4	8	83.714	N/A	4.5039	82.790	0.205
18	Ti-6-4	9	81.626	N/A	4.25	80.091	0.360
20	Ti-6-4	10	87.251	N/A	4.914	85.455	0.365
22	Ti-6-4 Heated	1	74.941	74.24	3.61	73.253	0.273
24	Ti-6-4 Heated	2	84.685	83.964	3.93	82.879	0.275
26	Ti-6-4 Heated	3	85.746	84.985	4.316	84.067	0.212
28	Ti-6-4 Heated	4	86.193	85.537	4.648	83.719	0.391
30	Ti-6-4 Heated	5	81.549	80.878	4.648	79.748	0.243
32	Ti-6-4 Heated	6	83.999	83.439	4.648	82.231	0.259
34	Ti-6-4 Heated	7	86.396	85.711	4.445	84.494	0.273
36	Ti-6-4 Heated	8	81.588	81.046	4.3125	80.189	0.198
38	Ti-6-4 Heated	9	84.848	84.131	4.648	82.945	0.255
40	Ti-6-4 Heated	10	84.886	84.252	4.504	83.049	0.267
42	Ti-6-4 ELI	1	69.73	N/A	3.811	67.272	0.644

44	Ti-6-4 ELI	2	69.933	N/A	3.8125	67.707	0.583
46	Ti-6-4 ELI	3	78.938	N/A	3.9375	77.572	0.346
48	Ti-6-4 ELI	4	73.948	N/A	3.813	70.709	0.849
50	Ti-6-4 ELI	5	75.241	N/A	4.25	73.999	0.292
52	Ti-6-4 ELI	6	73.304	N/A	4.00	71.1989	0.526
54	Ti-6-4 ELI	7	69.275	N/A	3.813	68.214	0.278
56	Ti-6-4 ELI	8	74.238	N/A	4.563	73.326	0.199
58	Ti-6-4 ELI	9	68.144	N/A	3.723	67.090	0.283
60	Ti-6-4 ELI	10	66.051	N/A	3.875	65.030	0.263
62	Ti-6-4 ELI Heated	1	70.391	69.558	3.367	68.277	0.380
64	Ti-6-4 ELI Heated	2	75.718	74.762	3.63	73.761	0.275
66	Ti-6-4 ELI Heated	3	64.369	63.694	3.281	62.875	0.249
68	Ti-6-4 ELI Heated	4	73.853	72.564	3.813	70.115	0.642
70	Ti-6-4 ELI Heated	5	73.537	72.713	4.125	71.916	0.193
72	Ti-6-4 ELI Heated	6	71.229	70.137	4.019	69.285	0.211
74	Ti-6-4 ELI Heated	7	76.343	75.667	4.426	74.674	0.224
76	Ti-6-4 ELI Heated	8	71.584	70.638	3.957	69.908	0.184
78	Ti-6-4 ELI Heated	9	70.163	69.166	3.875	68.151	0.261
80	Ti-6-4 ELI Heated	10	75.552	74.672	4.125	73.791	0.213

Table 7: Feeler Gauge Data

Sample Number	Inches Removed	Sample Number	Inches Removed	Sample Number	Inches Removed
1	0.007	**38**	0.004	**75**	0.0015
2	0.0015	**39**	0.0015	**76**	0.0015
3	0.013	**40**	0.005	**77**	0.0015
4	0.005	**41**	0.002	**78**	0.004
5	0.002	**42**	0.007	**79**	0.0015
6	0.005	**43**	0.002	**80**	0.002
7	0.004	**44**	0.004		
8	0.005	**45**	0.002		
9	0.002	**46**	0.002		
10	0.002	**47**	0.004		
11	0.002	**48**	0.005		
12	0.004	**49**	0.0015		
13	0.004	**50**	0.004		
14	0.004	**51**	0.002		
15	0.002	**52**	0.004		
16	0.002	**53**	0.0015		
17	0.006	**54**	0.0015		
18	0.005	**55**	0.002		
19	0.002	**56**	0.002		
20	0.004	**57**	0.0015		
21	0.005	**58**	0.005		
22	0.002	**59**	0.0015		
23	0.002	**60**	0.004		
24	0.0015	**61**	0.002		
25	0.002	**62**	0.004		
26	0.0015	**63**	0.004		
27	0.004	**64**	0.002		
28	0.005	**65**	0.003		
29	0.0015	**66**	0.002		
30	0.0015	**67**	0.004		
31	0.002	**68**	0.002		
32	0.004	**69**	0.002		
33	0.003	**70**	0.0015		
34	0.0015	**71**	0.0015		
35	0.002	**72**	0.002		
36	0.0015	**73**	0.0015		
37	0.003	**74**	0.0015		

Appendix B: Experimental Setup



Appendix C: Future Methodology

Newly Proposed Experimental Procedure

1. Gather required test pieces of equal size and shape.
2. Place half of the test pieces through the heating process and prepare for chemical milling.
3. Wear the proper PPE (lab coat, gloves, and glasses)
4. Clean and set up the fume hood for experimentation.
5. Prepare ice bath with approximately 800mL of water/ice in 2000mL beaker.
6. Fill rinse beaker (600mL) with water.
7. Fill 400mL test beaker with approximately 150-200mL of acid. Set up for agitation during testing.
8. Measure the surface area of the test piece (all should be the same).
9. Suspend the test piece in the acid via non-reactive basket or string.
10. Wait and observe the experiment for the given time (5 or 7 minutes). The bath should be agitated during this time.
11. Monitor the temperature for the control temperature and add ice if needed as the temperature rises due to the exothermic reaction.
12. Remove test piece from acid, allow excess acid to drip momentarily then dip the piece in the rinse bath for approximately 30 seconds.
13. Repeat steps 9-12 for the appropriate number of dips (3 or 4 depending on dipping time).
14. Rinse the Ti piece thoroughly and return it to the proper bag.
15. Record observations and clean all equipment and test area.

Appendix D: Microscopy Photos

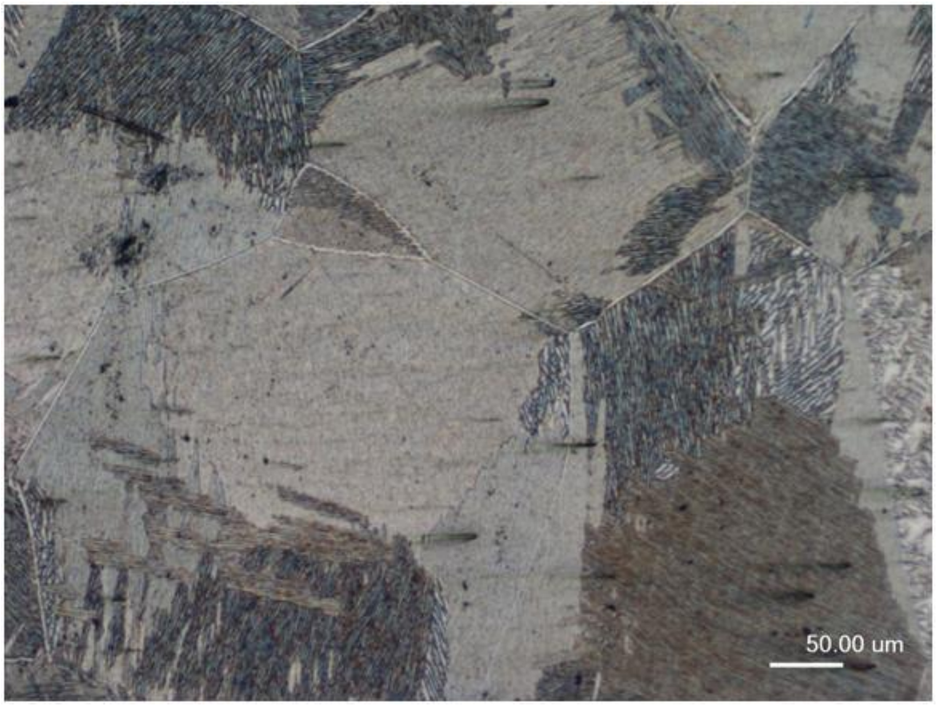


Figure 32: Ti-6-4 ELI, 5X Magnification

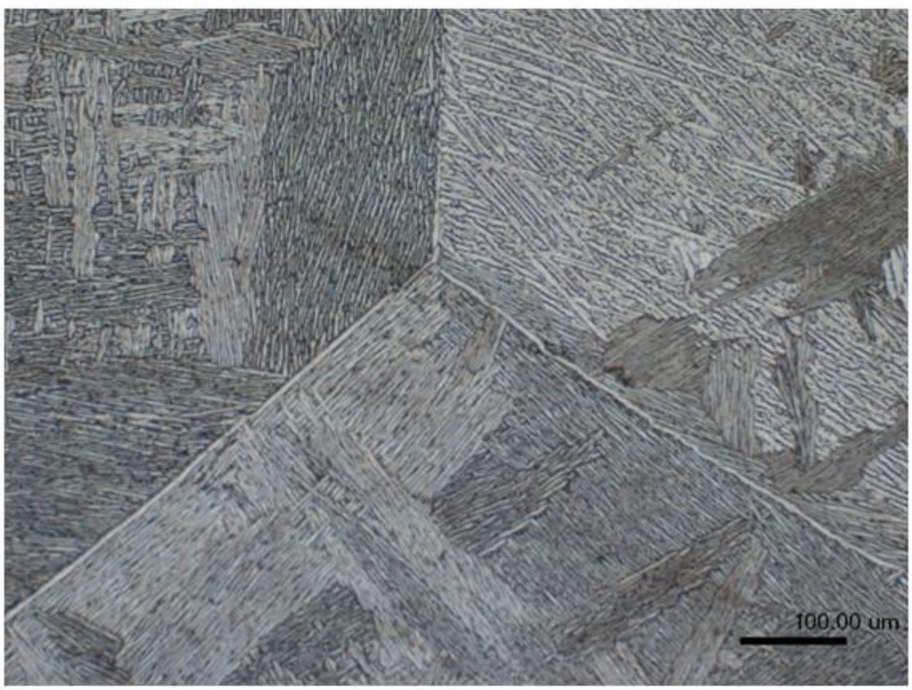


Figure 33:Ti-6-4 ELI, 10X Magnification

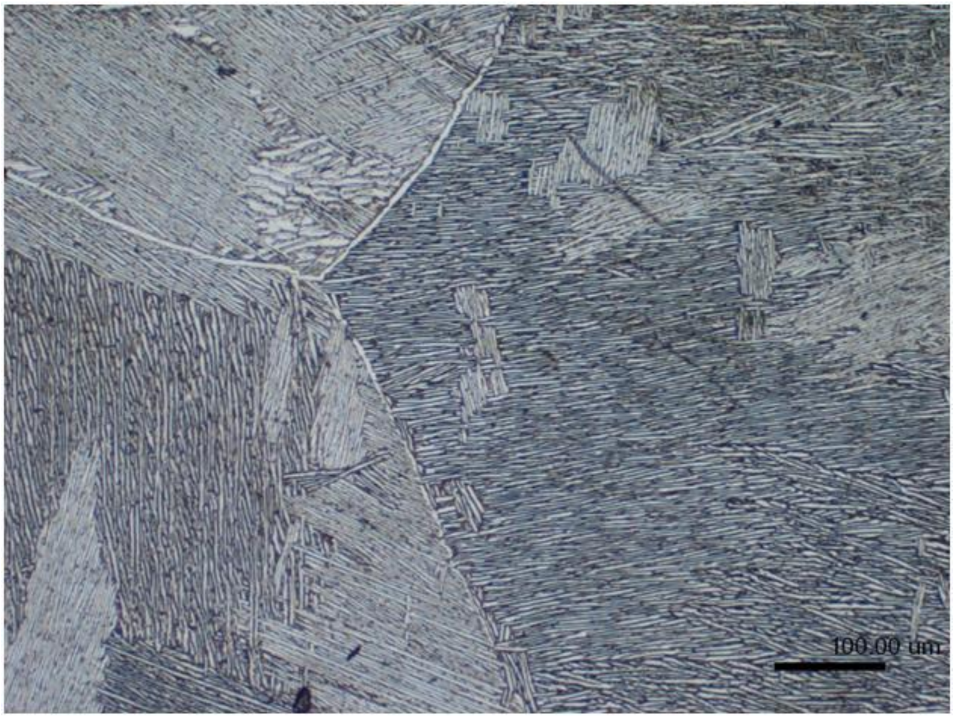


Figure 34: Ti-6-4 ELI, 10X Magnification , Second View

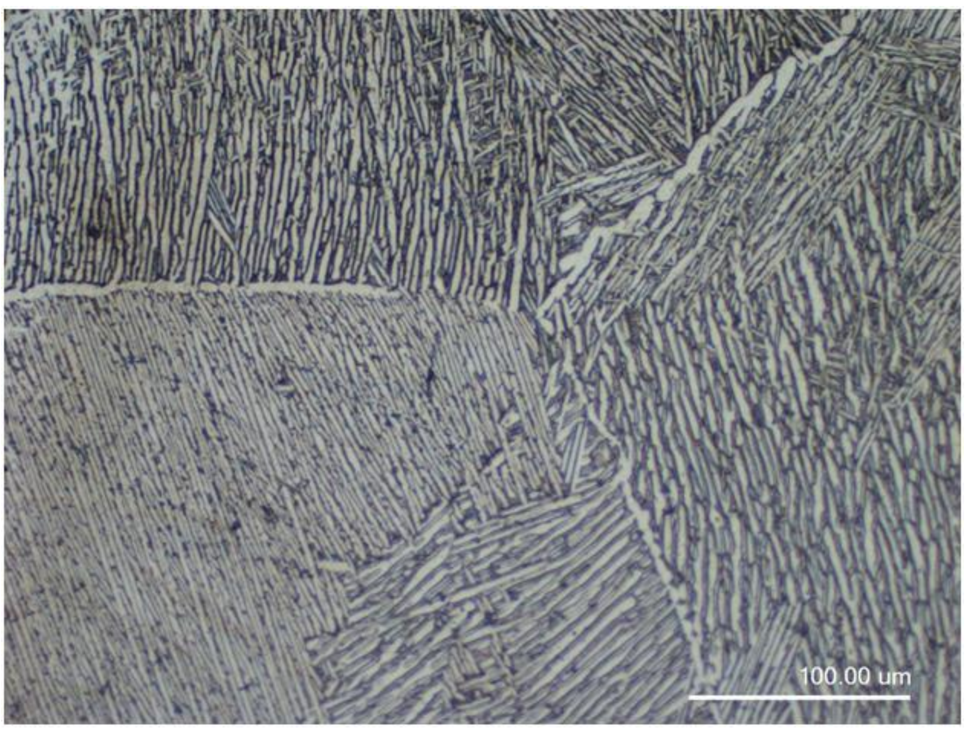


Figure 35: Ti-6-4 ELI, 20X Magnification

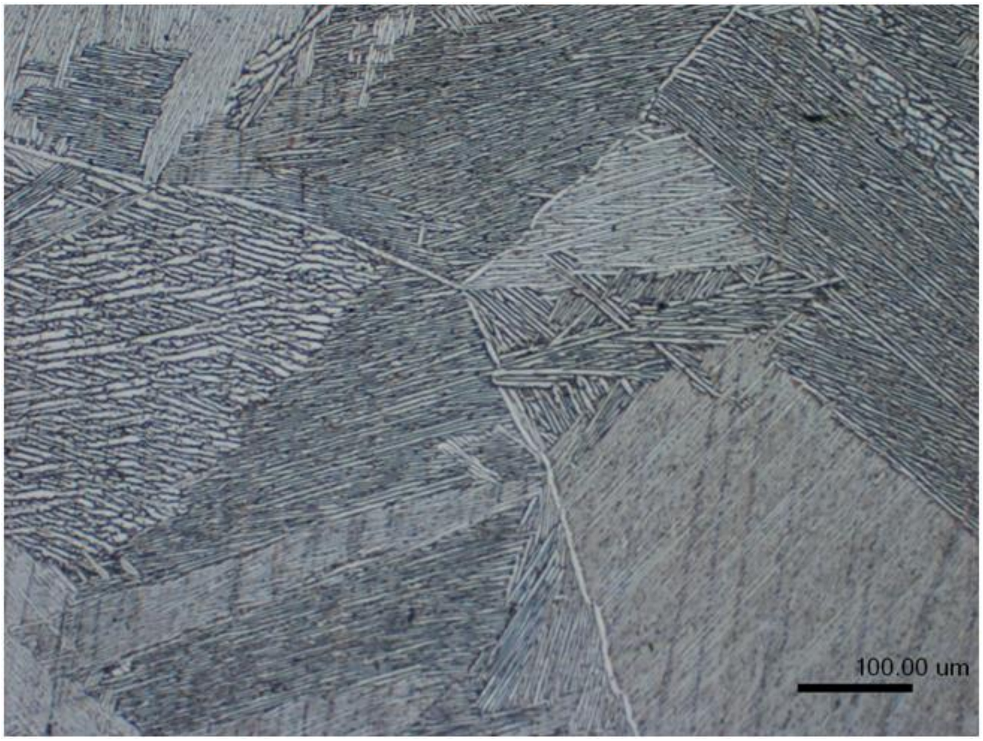


Figure 36: Ti-6-4, 10X Magnification

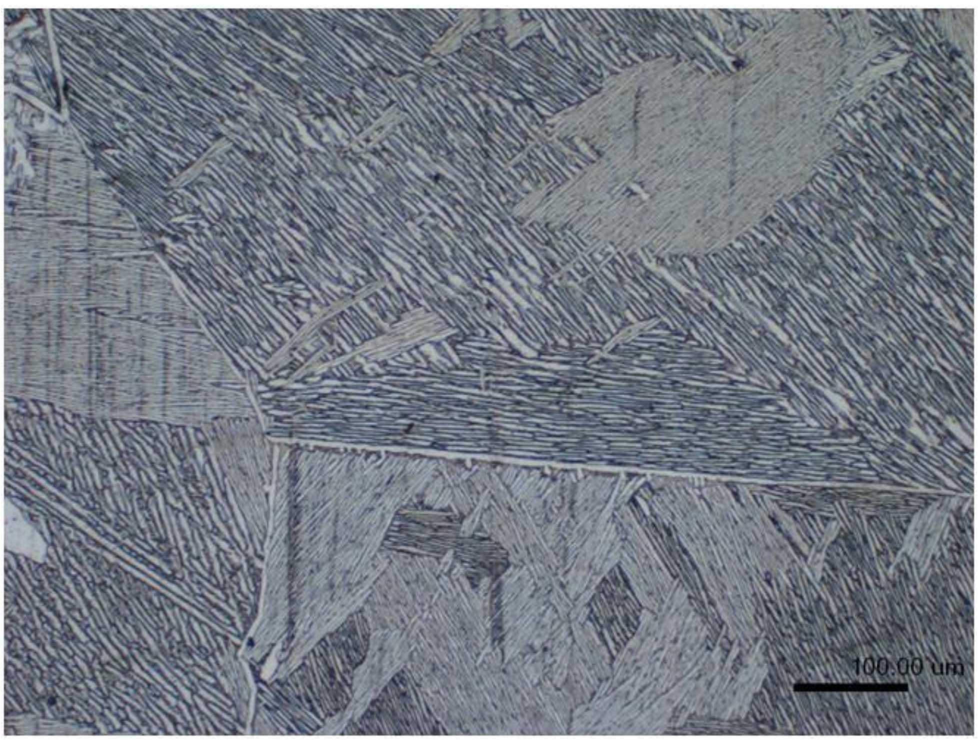


Figure 37: Ti-6-4, 10X Magnification, Second View

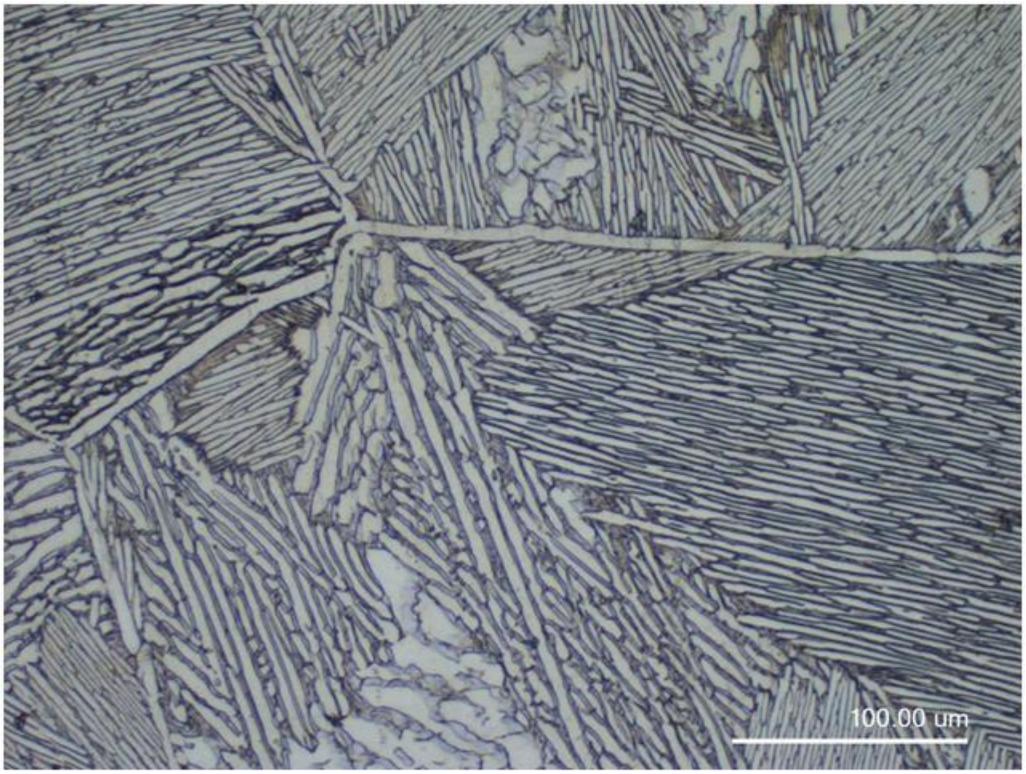


Figure 38: Ti-6-4, 20X Magnification