Titanium Alpha Case Prevention

A Major Qualifying Project report to be submitted to the faculty of
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Abstract

In an effort to more accurately predict diffusion kinetics of oxygen into titanium during heat-treatment, the Wyman-Gordon Company commissioned this study to obtain an accurate rate of alpha case formation within titanium and to investigate the use of coatings to reduce alpha case formation. This project consisted of heat-treating Ti-6Al-4V and Ti-6Al-4V ELI samples that were uncoated, coated with an SJ, and SJ advanced coating over a period of time consistent with their heat-treatment cycle. These samples were analyzed through optical microscopy and microhardness to determine alpha case depth. The project concluded with a cost analysis, which aimed to find the most economic and optimal solution to reducing alpha case formation.

Executive Summary

The Wyman-Gordon Company (WGC) is an industry leader in forging titanium aerospace components. Before the forging process can take place, these titanium pieces are heat treated in large gas furnaces. During the heat treatment process, oxygen diffuses into the titanium creates a stabilization of the alpha phase. This causes the formation of an alpha case layer. This alpha case layer is a hard, brittle shell. Its fragility makes it undesirable for aerospace applications. Titanium’s high strength to density ratio makes it ideal for the aerospace industry but formation of alpha case compromises this strength. Even a small fracture in the alpha case may cause a part to fail. Therefore, all alpha case formed during the heat treatment process must be removed through a chemical milling process involving corrosive acids: hydrofluoric and nitric. The objective of this project was to understand diffusion kinetics of oxygen into titanium during the heat treatment process in order to obtain an accurate rate of alpha case formation within titanium over time and to investigate coatings in an attempt to reduce alpha case formation.

To determine the rate of alpha case formation and compare a coating’s resistance to oxygen diffusion 12-piece sample sets of Ti-6Al-4V (Ti-6-4) and Ti-6Al-4V ELI (ELI) were heat treated under three coating conditions for a maximum of 6 hours and at 1750°F. The coating conditions were as follows:

1. Uncoated
2. Coated with SJ, current WG production procedure
3. Coated with SJ advanced

After heat treating the samples and performing the necessary preparation techniques of cutting, mounting, grinding, polishing, and etching each sample they were analyzed through optical microscopy and microhardness profiles. Using a microscope synchronized with a computer program we were able to photograph and measure the visible alpha case region on each sample under 20 times magnification. Microhardness testing was then performed to determine at what percentage range beyond the visible alpha case region the hardness profile of the sample

stabilized. This point indicated the minimum depth necessary to remove through chemical milling.

To visually represent the amount of alpha case formed and to compare the effect of each condition on alpha case formation, the optically measured depth was plotted against the square root of time each sample was heated. This representation showed a linear, positive correlation in the data thus indicating a parabolic growth of alpha case over time. The maximum average depth of alpha case observed was about 67 microns. Samples coated with SJ advanced showed a 37% reduction in alpha case on Ti-6-4 samples and a 54% reduction on ELI samples.

Microhardness profiles revealed that sample hardness did not stabilize until an average of 65% beyond the optically viewed depth of alpha case, with a maximum increase of 120%. The maximum depth of stabilization for Ti-6-4 samples was 110 microns and similarly 100 microns for ELI. With SJ advanced coated samples, however, the maximum depth before hardness stabilization was only 50 microns for Ti-6-4 and 30 microns for ELI.

After completing analysis upon our test samples and collecting data from WGC from the 2009 year a raw material cost comparison was conducted. It was found that by chemically milling only as much alpha case as was found through our analysis and by transitioning to the SJ advanced coating that a significant amount of money could be saved annually. Table 1 represents the potential savings associated with both these proposed changes.

Table 1: Cost Findings

	Current Process	Optimized Milling	SJ Advanced Coating
Coating Cost ($/yr)	$42,500	$42,500	$47,300
Acid Bath Cost ($/yr)	$688,000	$267,000	$172,000
Total Coating and Acid Cost ($/yr)	$731,000	$310,000	$219,000
Savings ($/yr)		**$421,000**	**$512,000**

Our results provide an accurate profile of alpha case accumulation on titanium for the WGC to reference when heating and milling. Optimizing the chemical milling process so that only the alpha case layer is removed would show immediate savings for WGC as their acid baths would begin lasting much longer. This would also benefit the company environmentally as less acid would need to be treated and disposed of, therefore lessening the risk of a spill. Furthermore, while the SJ advanced coating did not eliminate alpha case altogether, it did significantly reduce the amount of alpha case formed by protecting against oxygen diffusion. It is recommended that the WGC begin to use the SJ advanced coating in place of SJ. The project group recommends that our results be used to aid future research outside the scope of this project. In particular we recommend the following projects:

1. Determine coating durability and practicality within the forging process by simulating forging, cooling, and reheating cycles.
2. Investigate alternate methods of coating removal to further lengthen life of acid baths.
3. Continue experimenting with different coatings to completely prevent alpha case formation.

Acknowledgements

We would like to begin by thanking the WGC for allowing us access to their facility and equipment as we investigated the formation of alpha case over time and possible coatings to reduce the depth of contamination. In particular, we would like to thank Brian Postale and Briant Cormier for the creation of our project and for their continual discussion, interest, and assistance with becoming acclimated with the facility, equipment, and important people of interest that we utilized during at time at WGC.

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We appreciate the assistance of Advanced Technical Products in supplying our project group with a five gallon sample of the SJ advanced coating. Also, we would like to thank Roger Fabian of Bodycote Thermal Processing for being able to prepare a test sample under vacuum conditions for our group.

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Authorship Page

Justin Chretien, Matthew King, William Proia, and Stacy Rudolf all contributed to the outline and final edit of this research report. Each person's contributions in terms of authorship and editing are recorded on this page. Authors were responsible for writing an initial draft of each section. Editors revised, updated, and checked sections for appropriate voice, grammar, and mechanics.

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1 Introduction

Metals are plentiful natural resources that are and have been used in different technical applications throughout a variety of industries. Metals are extracted from ore and come in a raw form which must be manipulated to the correct shape and size for a specific application while maintaining desirable physical properties. One form of manipulation is hot metal forging, where metals are shaped by compressive forces while being exposed to high temperatures. Titanium is one such metal that is manipulated through hot metal forging at the Wyman-Gordon Company (WGC), a wholly owned subsidiary of Precision Castparts Corporation (PCC). The titanium which WGC forges is used in applications such as aerospace and defense to make aircraft parts and engines, and the strength of metal is imperative to the company's success. Although high temperatures are necessary for hot metal forging, it does cause a brittle layer to develop on the surface of titanium.

When titanium is exposed to high temperatures, a hard brittle layer caused by oxygen diffusing into the titanium, called an alpha case, is formed. Titanium is an incredibly strong metal; however, an alpha case layer reduces the amount of strain that the surface can withstand before cracking. If the metal cracks it creates a weak point in the metal that will eventually lead to part failure. This part failure could cause an airplane crash and the possibility of human casualties. There are three different possible ways to deal with alpha case formation on titanium: prevention, minimization, or removal. The current process at WGC for dealing with this issue is removal via chemical milling. Chemical milling consists of forged products being dipped into vessels filled with strong acids, hydrofluoric or nitric, to remove the alpha case. This current process is not an ideal solution to the problem because regulations in the industry cause chemical milling to be an expensive process to maintain. It also puts the company at legal risk in the unlikely situation where process safeguards fail and a chemical spill occurs that could harm employees, the surrounding community, or the environment. Further, the spent hydrofluoric acid has to be disposed of, causing further environmental concerns.

Extensive research has been completed to understand titanium alloys and the formation of the alpha case upon the heating of these alloys as is cited in the work of Lutjering & Williams.

Titanium has many qualities that make it ideal for use in aerospace and defense, and the reaction kinetics for the alpha case are explained in the work of Gurappa. Several studies have been completed to study the alpha case thickness at various heating temperatures and over different processes, including an experiment completed by Professor Richard Sisson of WPI. Studies of acid baths used for chemical milling have been assessed to remove the alpha case once it has formed. At the WGC, work has been done to optimize this process by assessing the amount of alpha case that forms at certain times and temperatures and studying how quickly the acid bath removes the alpha case so the titanium is milled with acid only long enough to remove the alpha case (Burnham & Dannheim, 1994). If the depth of alpha case is not correctly known, unnecessary milling will occur and the acid bath will become exhausted quicker than necessary. Other research has been completed by testing different coatings on the titanium to prevent or minimize the alpha case formation (Gurrappa & Gogia, 2001). At the WGC, work has been only been completed by testing different lubricants to aid the forging process including water-based or oil-based coatings (Cayer et al., 1997), no research has yet been focused upon coatings as a method for alpha case prevention.

While many studies have been conducted to better understand and predict the alpha case, there are still areas that need to be investigated to best deal with the alpha case formation at the WGC facility. The feasibility of different treatment methods for the titanium to prevent and minimize the alpha case has not been explored. Coatings besides the oil and water based lubricants have not been tested, and the economic impact such changes would have on the company have not been assessed. While the depth of the alpha case on the titanium alloys has been determined at various temperatures, an extensive study of this depth has not been conducted.

In this project, a comprehensive analysis of the depth of the alpha case formation over time was completed at the temperature and oxygen levels consistent with the forging process. A second purpose of this project was to determine if there are economically viable methods which could prevent or minimize the buildup of the alpha case on titanium alloys. Coatings were applied and the process conditions were varied to determine their effect on the alpha case buildup. If it is found that the alpha case can be prevented or minimized by using one of these methods, the WGC could reduce the amount of dangerous, expensive acids used to treat the remove alpha case. Finally, by understanding an in-depth analysis of the amount of alpha case formed, WGC can ensure that the titanium is not milled for longer than necessary to remove only the alpha case layer. The product of this research will aid in optimizing the current process, and could reduce or potentially eliminate the need for chemical milling altogether.

2 Literature Review

Any improvements made to the current operating conditions at WGC should take into account a full understanding of titanium, alpha case formation, and the titanium forging process. In this section, we provide a background to titanium and the various alloys and phases it is hold. Next, alpha case formation and prevention is discussed in detail. Finally, the current production process for titanium forging at WGC is outlined. This background information provides a solid foundation for which the methodology is based.

2.1 Titanium

Titanium is abundant on Earth. It is the ninth most prevalent element in the planet, and the fourth most prevalent metal within the Earth's crust (Moiseyev, 2005). The interest in Titanium sparked worldwide in the 1950's after World War II for its desirable properties, including its strength. Today, it is used mostly in the aerospace industry, but has applications in many others including medical prosthesis and automobile parts and engines (Avallone, Baumeister, & Sadeg, 2006).

Many properties make titanium an ideal metal for many applications. With its high strength to density ratio, Ti alloys are lightweight but still able to resist much stress and strain. In addition, it has a low coefficient for thermal expansion and high melting point making the metal ideal for operations over 50 degrees Celsius (Lutjering & Williams, 2003). Titanium also has a low electrical resistivity (Boyer, Collings, & Welsch, 1994). In addition, titanium reacts readily with oxygen to form a hard and brittle layer, called the alpha case layer, over the metal making it extremely resistant to corrosion. The layer is stable enough that hydrofluoric acid is one of the only acids that can break it apart (Moiseyev, 2005).

While titanium has many desirable properties for many uses, there are also problems preventing it from being used for many applications. Because titanium readily reacts with oxygen, it is very difficult to purify. The Kroll process, developed in the 1930's, is still used today to isolate titanium (Lutjering & Williams, 2003). Rutile (TiO_2) and ilmenite ($FeTiO_3$) are mined, and then treated with chlorine to create TiCl4 (Avallone et al., 2006). This compound then needs to be treated in an inert or vacuum environment to obtain a Ti sponge, named for its spongy appearance. The complicated purification process makes the metal very expensive. Further, at temperatures greater than 600 degrees Celsius, a brittle oxide layer quickly forms (Lutjering & Williams, 2003).

2.1.1 Titanium Phases

Titanium exists in two phases, an alpha phase usually exhibited at room temperature, and a beta phase as it is heated. Each phase contributes to different properties of titanium and titanium alloys. A phase diagram of titanium is shown below in Figure 1 (Gale & Totemeier, 2003).

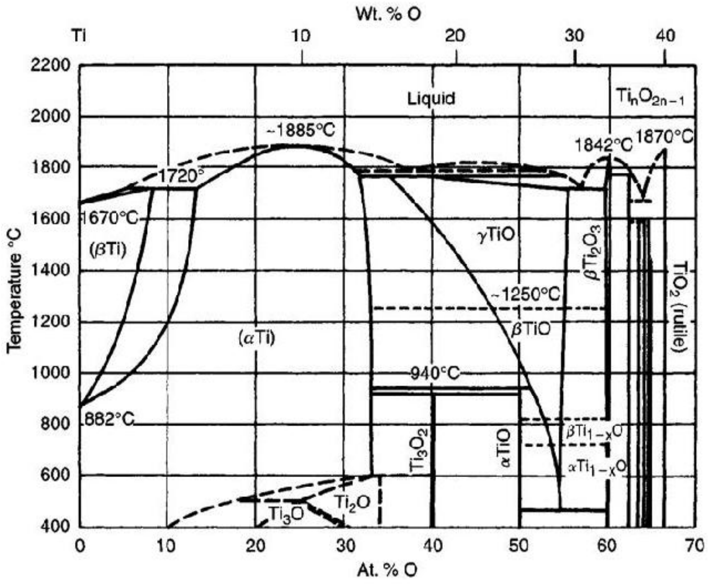

Figure 1: Titanium Phase Diagram (Gale & Totemeier, 2003)

The alpha phase is stable at room temperature, and thus, is the phase of pure titanium under standard conditions. Even at low temperatures, this titanium phase is ductile, thermally stable, and yields weldability (Moiseyev, 2005). It has a hexagonal close packed structure (HCP) (Lutjering & Williams, 2003) as shown below in Figure 2 (*Crystal structure*.2009).

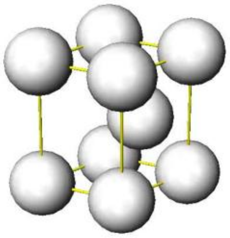

Figure 2: Hexagonal Close Packed Structure (Callister, 2006)

Alpha titanium is anisotropic, meaning the HCP molecule has different angles associated different directions within the molecule (Callister, 2006). This anisotropy affects the elastic modulus, E, at different angles (Lutjering & Williams, 2003). In general, a larger E value indicates a stiffer material with greater resistance to elastic deformation (Callister, 2006). Aluminum can be used to interstitially stabilize the alpha structure making the titanium more ordered with more covalent bonds, increasing E (Lutjering & Williams, 2003).

At high temperatures, alpha titanium will convert to beta titanium, with a body centered cubic (BCC) structure, as seen below in Figure 3 (*Crystal structure.*2009).

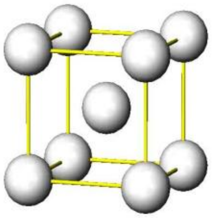

Figure 3: Body Centered Cubic Structure (*Crystal structure,* 2009)

The transformation takes place at 882 degrees Celsius in pure titanium, but can be higher or lower depending on the alloy. The beta phase has a lower E value than alpha titanium, and is not stable at room temperature. However, if at least 15% vanadium (V) is introduced into the metal, the beta phase becomes stable at room temperature. Unlike Al, V disturbs the bonding force of the titanium lattice, and decreases the value of E (Lutjering & Williams, 2003). A compound with both the alpha and beta phases creates a titanium compound with greater ductility, strength, and high temperature strength than pure alpha titanium (Moiseyev, 2005).

2.1.2 Titanium Alloys

Titanium alloys are used to create the properties desired for different applications. Alloying elements dissolve into the phases and increase the atom to atom interactive forces, making the compound more stable than pure titanium (Lutjering & Williams, 2003). In general, alloying elements increase the strength but decrease the ductility of titanium (Moiseyev, 2005). Each alloying element can be classified as an alpha or beta stabilizer, and alloys can be classified as alpha alloys, beta alloys, or alpha and beta alloys depending on the phases present in the alloy. These alloying elements also affect the transition temperature of the titanium (Lutjering & Williams, 2003).

The alpha phase is stabilized by a variety of elements including: aluminum, gallium, germanium, carbon, oxygen and nitrogen. Of these, aluminum is the most practical. It is very soluble in both the alpha and beta phase, and is the only common metal to raise the transition temperature (Lutjering & Williams, 2003).

Beta stabilizers can be classified as eutectoid or isomorphous. Eutectic beta stabilizers have mixtures with the titanium such that the melting point is at a local temperature minimum, while the isomorphous stabilizers have complete liquid and solid solubility in the beta titanium (Callister, 2006). Several common eutectoid stabilizers are: Cr, Fe and Si, and several common isomorphous stabilizers are: V, Mo, and Nb. Vanadium is the most practical of the beta stabilizers. As an isomorphous compound, it readily dissolves into the beta phase. It is also more soluble than the other isomorphous stabilizers in the alpha phase. Conventional Ti alloys have a maximum amount of 15% V (Lutjering & Williams, 2003).

The most common of the Ti alloys is Ti-6Al-4V (Ti-6-4), named as it contains 6% aluminum and 4% vanadium. It accounts for 50% of Ti tonnage worldwide, 80% of which is used by the aerospace industry (Boyer et al., 1994). WGC uses this alloy. Its transition temperature is 800 degrees Celsius, and at room temperature the mixture is 15% beta titanium. It is made by heating titanium and then cooling rapidly by quenching in water to form a martinsitic crystalline structure. The alloy has a balance of strength and ductility, and resists fatigue and fracture propagation. However, it is only useful to about 300 degrees Celsius (Lutjering & Williams, 2003). It can be made in many forms including: wrought, cast, or powder metallurgy form. Wrought titanium is always used for aircraft parts. In the industry, the alloy is typically used in mill annealed conditions (Boyer et al., 1994). Thus, the metal is heated for a prolonged period and slowly cooled (Callister, 2006). In order to treat the spaces that form in the metal known as porosity, the metal castings are usually pressed with heat and high pressure (Boyer et al., 1994).

Though Ti-6-4 titanium alloys are the preferred metal for aerospace applications, there are still problems than can arise from stresses the metal is exposed to. If the alloy is exposed to hydrogen, hydrogen damage may ensue. The result is a loss of ductility and a reduced stress/intensity threshold for crack propagation. At temperatures of about 300 to 350 degrees Celsius, creep becomes a concern with titanium alloys (Boyer et al., 1994). Creep is caused when high temperatures and static mechanical stresses result in deformation (Callister, 2006). It can be best resisted with near alpha alloys, and can be prevented with treatment. Fretting fatigue is an additional concern. Thus, if the metal slides against itself or other materials, the titanium alloy exhibits poor wear resistance. Further, the high cycle fatigue strength is lowered during annealing, but can be improved by rapid cooling. However, the rapid cooling process produces a much harder, martensitic, variation of the alpha phase not desired in the alloy (Boyer et al., 1994).

Ti-6Al-4V ELI (ELI), extra-low-interstitial, is a tougher and more ductile form of Ti-6-4. It is a slightly purer alloy of titanium. It contains 11% oxygen and 10% nitrogen as opposed to regular Ti-6-4 which contains 18% oxygen and 15% nitrogen. The reduction of the amount of dissolved gases gives ELI the increase in toughness and ductility at the cost of its yield strength (Boyer et al., 1994). The similarities in composition and increased toughness and ductility, make this alloy a compatible filler metal for welding Ti-6-4.

ELI has a variety of applications. It is used commonly in a wide variety of surgical implants. It is also used to make high pressure and low temperature equipment due to its retained toughness in such conditions. High pressure cryogenic vessels are an example of this.

2.2 Heat-treatment of Titanium

The most common heat-treatment of titanium is to fully anneal the metal. It undergoes STA (solution treated and aged) to improve is strength. By annealing the metal, the beta phase is best preserved to increase the fracture toughness and decrease the crack growth. However, the presence of the beta phase lowers the ductility of the metal or alloy. By creating the presence of both the alpha and beta alloys when hot-working, coarsening that results from having only the beta phase can be prevented (Boyer et al., 1994).

Several measures can be taken to improve the high temperature strength of the titanium alloys. The first of these treatments is cold-work hardening. It is caused by the deformation of the metal at temperatures lower than the recrystallization temperature. However, this lowers the elastic modulus, and limits the range of temperatures at which the titanium can be used. It can also be fused with components to form solid solutions with basic metals. While this increases the strength, it also increases the stability of the compound to the point that it significantly decreases the transformation from the alpha to beta phase in heat-treatment. Other options include fusing the titanium with various elements or forming a mixture of phases (Donachie, 2004).

2.3 Alpha Case Overview

The alpha case is a “thin, hard, brittle surface layer” that is created during the forging process as liquid titanium interacts with oxygen (Keanini, Watkins, Okabe, & Koike, 2007). Occurring at temperatures greater than 600°C, the reaction kinetics allow approximately 33 percent of the atmospheric oxygen to dissolve in the exposed liquid titanium surface. Once solidification occurs, this layer, while not affecting the properties of the interior titanium alloy, greatly reduces the structural integrity of the titanium as tensile ductility and fatigue resistance are compromised (Gurappa, 2003). Therefore, if left untreated this alpha case layer will cause the titanium alloy to fail in its application much sooner than if no alpha casing was present.

2.4 Dominating Factors

The most dominating factors in alpha case formation are oxygen, time, and temperature (Gurappa, 2003). Since oxygen readily diffuses into liquid titanium at high temperatures, as the amount of atmospheric oxygen is increased, the alpha case layer becomes more defined. Similarly, at greater time intervals and temperatures the alpha case layer becomes more pronounced. I. Gurappa, a scientist at the Defense Metallurgical Research Laboratory of India, conducted a study to determine the depth of alpha casing in regards to time and temperature. Figure 4 (Gurappa, 2003) shows the predicted depth of alpha casing with respect to increasing time and temperature. As shown over a set period of time, temperature has a significant effect on the alpha case layer.

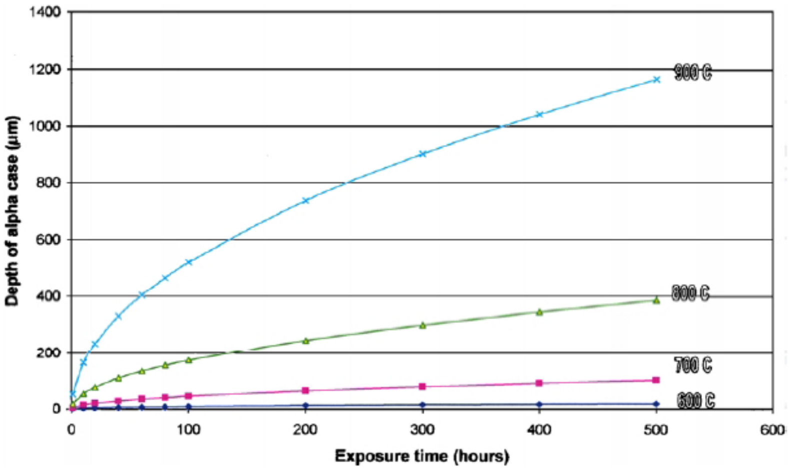

Figure 4: Predicted depth of α-case for titanium alloy IMI 834 at different exposed temperatures (Gurappa, 2003).

Figure 5 (Gurappa, 2003) shows a similar graph, however the alpha case depth is reported as a function of microhardness. At 600°C the depth is a minimum at 25 µm. A slight increase is seen with a minimum of 50 µm at 700°C. Finally at 900°C a drastic increase to 140 µm is observed.

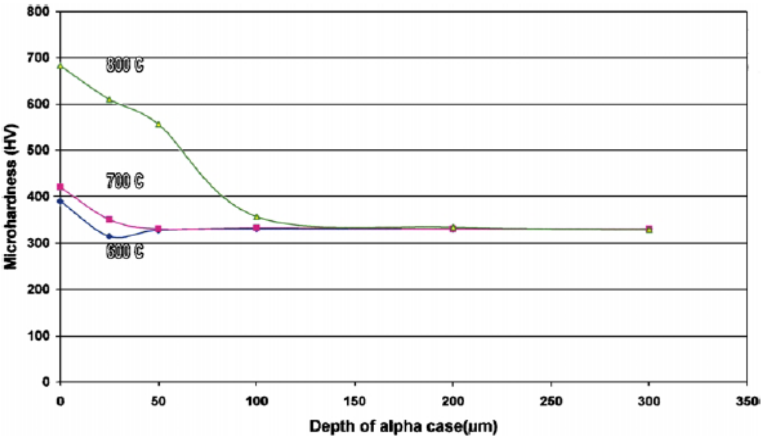

Figure 5: Measured microhardness profiles of titanium alloy, IMI 834, after 100 h of oxidation at various temperatures showing the depth of α-case (Gurappa, 2003).

2.4.1 Theoretical Calculations

In one recent, R.G. Keanini, professor at the University of North Caroline at Charlotte, examined the thermophysical features of small scale titanium forging process. These features include: induction period, solidification rate and time, and the corresponding alpha case depth (2007).

From the time the first Ti liquid drop touches the casting mold an induction period, τ_I, exists where those surface and air constituents diffuse uniformly into the titanium before solidification begins. At the end of this induction period the liquid titanium begins to solidify and the diffusion of material into liquid ceases. The alpha case layer can then be calculated knowing the thermal diffusivity of the titanium, α, as follows: $\delta = \sqrt{\alpha \tau_I}$ (Keanini et al., 2007). These results show that the "magnitude of the bulk contaminant concentration is almost certainly determined by a combination of the length of the induction period, τ_I, as well as by the chemical makeup of the mold" (Keanini et al., 2007) and amount of oxygen present.

2.5 Alpha Case Prevention

Titanium and titanium alloys have the distinct advantages over other metals by having properties with an excellent yield strength, corrosion resistance, fatigue resistance and biocompatibility. Therefore, most work with titanium has been aimed at cost reduction rather than increasing property specifications. This rational is described as follows, "From a viewpoint of cost efficiency, the investment casting of titanium alloys could be the most economic net-shape technology rather than permanent mold and vacuum die-casting, because the investment casting allows complexity, prototype, rapid cooling and high reliability" (Sung, Choi, Han, Oh, & Kim, 2008). The potential for cost savings during the Ti casting process has led to recent research throughout the metallurgical community to determine methods of reduce alpha casing without the use of vacuum die-casting. Two such methods, described in the following sections, took into account various molds and coating.

2.5.1 Molds

Ceramics such as calcium oxide (CaO), zirconium oxide (ZrO_2), zirconium orthosilicate ($ZrSiO_4$), and aluminum oxide (Al_2O_3) have been used as mold materials to eliminate the formation of an alpha case layer as they thermodynamics do not favor titanium oxide (TiO_2) formation. TiO_2 has a more positive standard free energy of formation of oxides and therefore will not proceed spontaneously (Sung & Kim, 2005). However, Figure 6 (Sung et al., 2008) shows that when used as a mold these alpha case layers still do exist when viewing the hardness profile of the material. A consistently formed alpha case layer with minimum thickness at 250 µm is seen for all materials except Al_2O_3, which has a minimum thickness at about 500 µm. Therefore, it is evident that an unpredicted chemistry is occurring during this process.

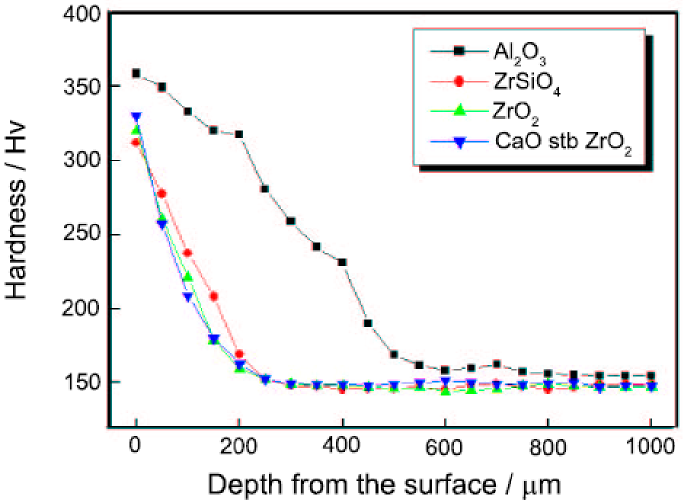

Figure 6: Hardness profiles with mold materials: Al_2O_3, $ZrSiO_4$, ZrO_2 and CaO stabilized ZrO_2 (Sung et al., 2008).

Based upon the thermodynamics the reaction between titanium and Al_2O_3 should not produce alpha case spontaneously during the forging process. The explanation for the alpha case region can be explained through the element mapping images of Figure 7 (Sung et al., 2008). These images show that the mold material, aluminum, dissolved into the titanium and ultimately affected the reaction, as seen by the green band within the Al quadrant of Figure 7. In this instance, the aluminum is primarily responsible for the alpha case layer which is composed of both TiO_2 and titanium aluminide (Ti_3Al). Therefore, a conclusion as to the mechanism for alpha case formation can be drawn, "…it could be confirmed that the *alpha case* is formed by not only interstitial oxygen atoms but also substitutional metal atoms dissolved from mold" (Sung et al., 2008).

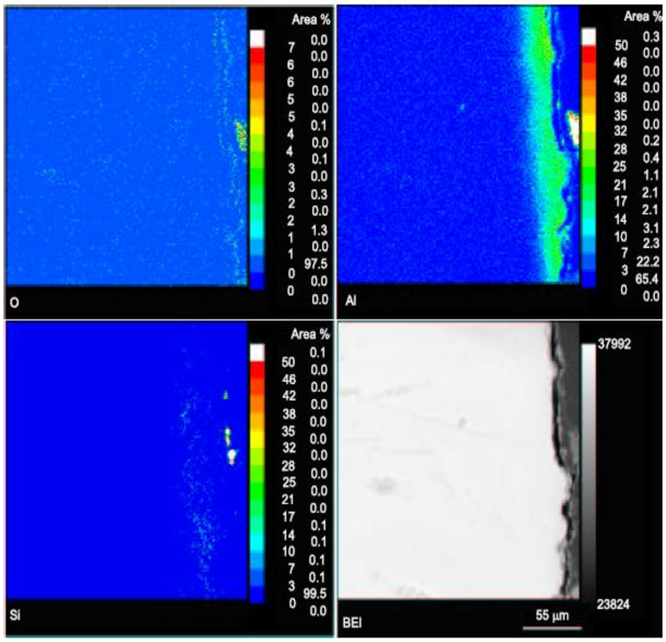

Figure 7: Comparison of elemental mapping images of O, Al and Si in Ti castings into Al2O3 mold and backscattered electron imaging (BEI) image (Sung et al., 2008).

Since it was determined that atoms from the mold materials could facilitate an alpha case layer, alpha case control molds are constructed of the materials TiO_2 and $TiAl_3$, the products that cause alpha casing from the Al_2O_3 mold. By utilizing alpha case control molds the alpha case layer can be prevented as the titanium aluminide reaction does not occur. The result is a uniform hardness profile as shown in Figure 8 (Sung et al., 2008).

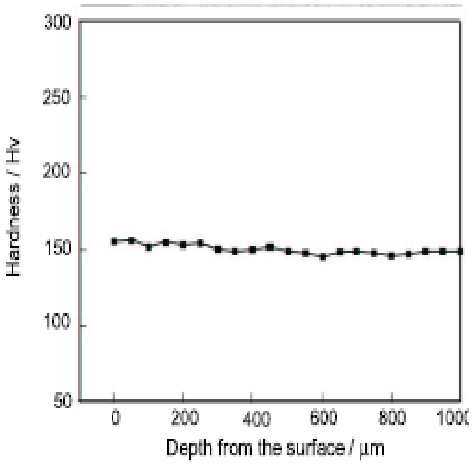

Figure 8: Hardness profile between pure titanium and alpha case controlled mold (Sung et al., 2008).

2.5.2 Coatings

When exposed to temperatures greater than 500°C oxygen readily diffuses into titanium to create an alpha case layer. It is necessary to reduce that absorption of oxygen in order to more efficiently forge at higher temperatures since in general alpha casing is proportional to temperature. Ceramic coatings cannot be utilized as they have too low a malleability and are not stable at the high temperatures necessary to forge. Metallic coatings are more stable at higher temperatures; however have the tendency to diffuse metallic particles to the titanium and therefore produce a contaminated alpha case layer (Gurrappa & Gogia, 2001).

As an alternative, sodium silicate (Na_2SiO_3) is often applied to titanium as an oxygen barrier coating to prevent alpha case formation. In one study performed by S.N. Patankar et al., Na_2SiO_3 was applied to Ti-6-4. The result shows an ultimate tensile strength (UTS) and yield strength relatively unaffected by application of the Na_2SiO_3 coating, as shown in Figure 9 (2001). The only negative effect from the coating was that was an increased ductility. Since this coating was able to prevent alpha casing, retained its original finishing, and retain most physical properties, this coating seems feasible to be applied to Ti before forging provided ductility is not of major concern.

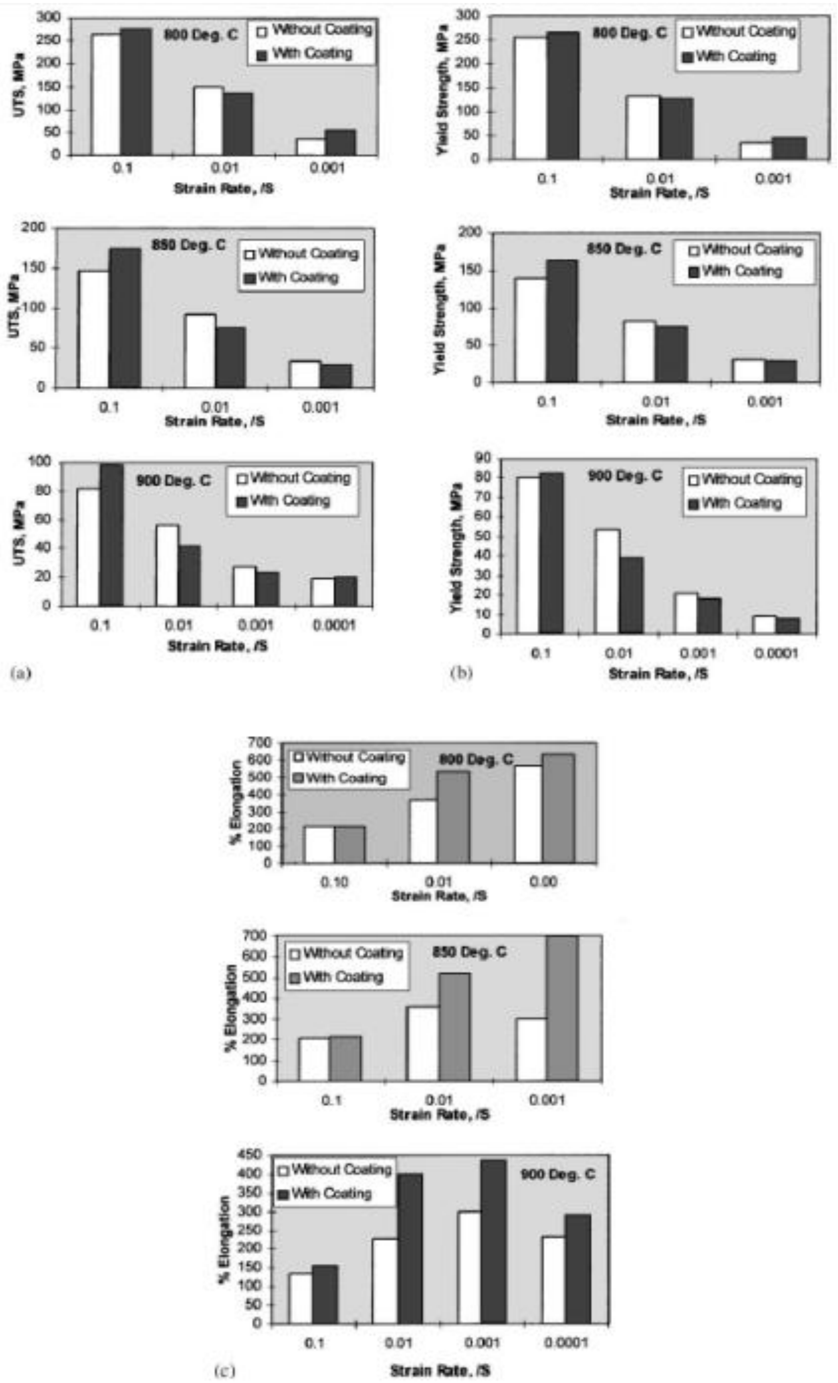

Figure 9: Variation of (a) UTS, (b) yield strength, and (c) ductility as function of strain rate (S.N. Patankar et al., 2001).

Another common coating used for titanium gas-turbines is platinum aluminide. A comparative study of the oxidative effects upon an uncoated, plain aluminide coated, and platinum aluminide coated titanium alloy, as shown in Figure 10 (Gurrappa & Gogia, 2001), demonstrates a drastic variation in alpha case creation. These results show a reduction in weight gain of more than 60% through the plain aluminide samples and an even greater reduction, almost 95%, through the use of the platinum aluminide coating. Both show drastic improvements over an uncoated sample.

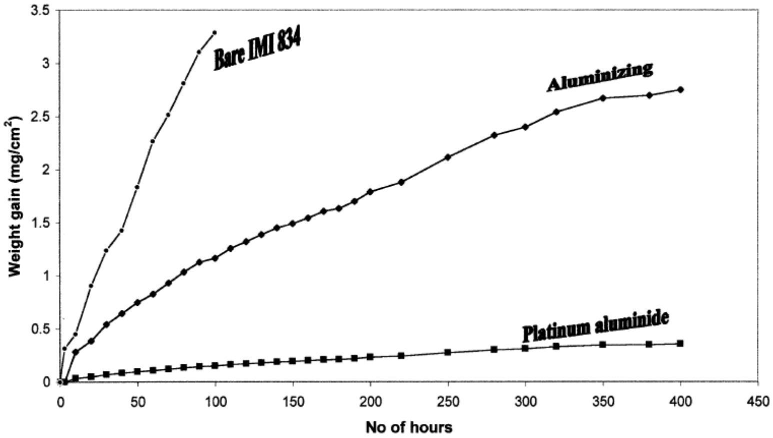

Figure 10: Cyclic oxidation kinetics of titanium based alloy, IMI 834 with different coatings at 800°C and comparison with the uncoated alloy (Gurrappa & Gogia, 2001).

Through the use of an electron microscope, a cross sectional view of the materials can be obtained, as in Figure 11 (Gurrappa & Gogia, 2001). The plain aluminide coating is shown to have a slight amount of oxidation while the platinum aluminide contains even less. Notably, both coatings successfully prevented alpha case formation altogether. In contrast, the uncoated titanium alloy is layered with both an oxidization and alpha case layer.

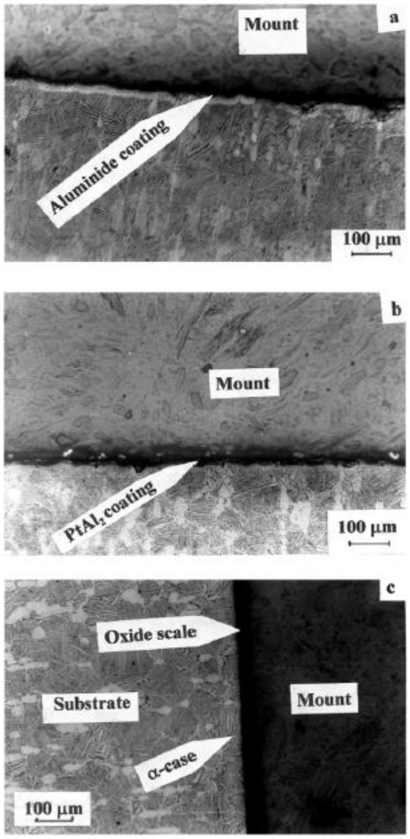

Figure 11: Cross sections of titanium alloy heated for 100 hours at 800°C in air with (a) plain aluminide, (b) platinum aluminide, (c) bare titanium alloy (Gurrappa & Gogia, 2001).

3 Methodology

The goals of our Major Qualifying Project were: to create a profile of alpha case formation for Ti-6-4 and ELI over a period of time, and determine any alteration of process conditions or addition of a coating that would prevent or reduce alpha case formation. We identified four major objectives which will aid us in the pursuit of our goals and associated tasks which must be completed in order to achieve each objective. The objectives were:

1) Determine parameters to be tested and data to be collected
2) Create alpha case samples and prepare for analysis
3) Analyze alpha case depth on sample by microscopy and microhardness
4) Develop functional deliverables to represent alpha case depth over time

3.1 Create alpha case samples and prepare for analysis

The following sections outline the procedural steps for creating alpha case on our test pieces as well as preparing them for analysis.

3.1.1 Creating Alpha Case

Titanium alloy samples were obtained from the test prep department at WGC. These samples were 1 in. x 5 in. rectangular prisms and did not have any alpha case. Each sample was heated in electric furnace 5217 located in the heat-treatment area at WGC. Twelve samples of Ti-6-4 and ELI uncoated and coated were heated over a length of six hours where one sample was removed every thirty minutes. This time period was chosen to as it is the average heat-treat time for the titanium forging process. This process created conditions consistent enough to create a profile of alpha case formation for each category of sample. Ti-6-4 and ELI were chosen as the titanium grades to test because they are the most commonly used in aerospace application and are the two most forged grades that WGC sells.

3.1.2 Cutting Samples

After each sample had been heated and forged there was consequently alpha case present. We cut each sample in order to expose a cross section at which the depth of alpha case could be examined using various analytical techniques. Each sample needed to be smaller than one cubic inch. Cutting samples of titanium alloy with alpha case can be a lengthy task since the alpha case is much harder than the titanium itself. Thus, a lab saw with a titanium alloy blade was not sufficient to make all cuts necessary to reduce the sample to at least smaller than one cubic inch. The test prep department at WGC was able to cut each sample to the cubic inch size and then we used the Mark V Series 600 saw in the Washburn shops to make the final cut which reduced the size of the titanium sample below one cubic inch.

3.1.3 Mounting, polishing, and etching

In order to perform the necessary testing on the cut samples of titanium they had to be mounted. The main purposes for mounting samples were to assist in handling the small pieces during examination and to preserve the oxide and alpha case layers on the edges of the samples. A phenolic powder was placed around the sample using an automatic mounting press. Upon pressurizing and heating the powder, it melted and formed a plastic case around the titanium sample without affecting the sample whatsoever (Buehler, 2007).

The next step in sample preparation was polishing the mounted sample in order to accurately and clearly view the microstructure and alpha case depth. The objective was to produce a sample that is “scratch free and mirror-like in appearance” (Buehler, 2007). Our titanium samples were initially polished using a manual technique on the Buehler MetaServ 2000 grinder/polisher. The sample was rotated opposite the direction the polishing wheel was spinning so as to polish in more than one direction along the sample. The next polishing step required an aqueous alumina solution of 1.0 then 0.05 microns to ensure a smoother surface finish on the sample. The final polishing abrasive utilized the MasterMet colloidal silica polishing suspension. This bettered the finish by a chemical action which is beneficial to samples more difficult to prepare, such as titanium. The final step was ultrasonic cleaning, necessary to remove unwanted debris for minute cracks or pores.

The final step in sample preparation was to chemically etch the sample with an acid solution. The acid used was a mixture of ethanol and 3% nitric acid, known as nital. This etchant was used to more prominently define and improve the contrast between the boundary layer of the alpha phase and the alpha-beta phase. The acid was applied with a cotton swab for 10-15 seconds and then rinsed in water to stop the etching from continuing. A second etching was performed using a more selective acid solution as a way of comparing the effectiveness of the nital solution.

This acid solution, known as Kroll's Reagent consisted of 92 mL water, 6 mL nitric acid, and 2 mL hydrofluoric acid.

3.2 Determine parameters to be tested and data to be collected

The following sections describe the parameters and variables taken into account while testing.

3.2.1 Parameters varied

The main parameters which were varied during the heating operation included the time the sample was left in the furnace, the temperature of the furnace, the grade of the titanium alloy, presence and type of coating, and presence of reheat cycle.

3.2.2 Data recorded

Time, temperature, and the depth of alpha case formed were the most important data collected after the heating operation. This data made it possible to create a time, temp, and depth profile for each category of titanium alloy. In addition to examining the bare alloy, some samples were coated and tested with the same process. A testing matrix was developed so that the data could be recorded for each alloy, coating type, and thickness.

3.3 Analyze alpha case depth on samples

The following sections define the steps taken to analyze each sample and collect our data.

3.3.1 Optical Microscopy

The depth of alpha case diffused into each titanium sample was measured using a Nikon Epiphot optical microscope at 20x magnification. The microscope was connected to a computer which used the ACT-2U program in order to measure the alpha case, based upon the micrometer scale of magnification, and to capture images of each sample. The alpha case was easily recognizable as a brighter, white layer that occurred along the surface. It was necessary to view each side of the samples to determine which had alpha case diffused into them. When measuring the alpha case, five separate readings were taken within the microscope view and averaged to determine the average alpha case depth along the side.

3.3.2 Micro-hardness analysis

The true depth of the alpha case cannot be seen completely when taking pictures with the microscope. The oxygen diffuses further into the sample than is visible as described by the alpha-beta phase. Thus, to obtain a more accurate measurement of the alpha case and to estimate the error in our visual readings, microhardness testing was performed using the Shimadru HV-2000 Microhardness Tester. Samples were placed in the microscope, and measurements were made using the Vickers Microhardness scale. The first imprint was made on the edge with alpha case of each sample, and subsequent imprints were made approximately a half of a diamond length toward the center of sample until the hardness readings were consistent. The test was performed on the six samples that remained in the furnace for six hours.

3.4 Cost Analysis

To determine whether it would be economically beneficial for the WGC to optimize their milling process and implement usage of a new coating a cost analysis was performed. A proportional cost analysis was used to obtain an estimate of savings. To perform these calculations it is necessary to gather the following key points of information.

1. Average life of acid bath
2. Cost of acid bath
3. Average depth milled off Ti surface
4. Quantity of SJ coating ordered per year
5. Cost of SJ and SJ advanced coating

Based upon the reduction in alpha case via optical microscopy and microhardness data between the samples applied with the SJ and SJ advanced coating a proportional comparison was made to determine how much longer the acid bath could be kept before changeover. This longer bath life was then be compared to the optimized milling conditions and the increase cost of the SJ advanced coating to determine the overall cost benefit.

3.5 Vacuum Testing

To act as a best case scenario comparison, an uncoated sample of Ti-6-4 was tested as Bodycote to compare alpha case formation under vacuum conditions as opposed to atmospheric oxygen conditions. This sample also underwent microscopy and microhardness testing to determine how atmospheric conditions affect alpha case formation.

4 Results and Discussion

This section discusses the results from the data collected as described in the preceding Methodology section. The first subsection describes how the alpha case region was identified during microscopy. The second subsection assesses the alpha case depth trends through both optical microscopy and microhardness profiles. The third subsection identifies potential cost savings by implementing a new type of coating that reduces alpha case formation. The fourth subsection compares and contrasts the SJ advances coating to the SJ coating currently used at WGC. The final subsection addresses some limitations we encountered throughout the project. Although we were only able to test on a small scale compared to the titanium pieces that WGC typically forges, we believe the trends we found will remain similar regardless of samples size.

4.1 Optical assessment of heat-treated specimens

We visually investigated each heat-treated sample using an optical microscope in Washburn Laboratories at WPI. The alpha case region was identified by noticing a lighter region adjacent to the outer edge of the sample. The following results show two methods we used to identify the alpha case region for each sample.

4.1.1 Phase contrast

The first difference we noted between alpha phase and alpha-beta phase was a difference in contrast. As seen in Figure 12, the alpha case region was a lighter shade in contrast than the alpha-beta region and therefore able was measured optically.

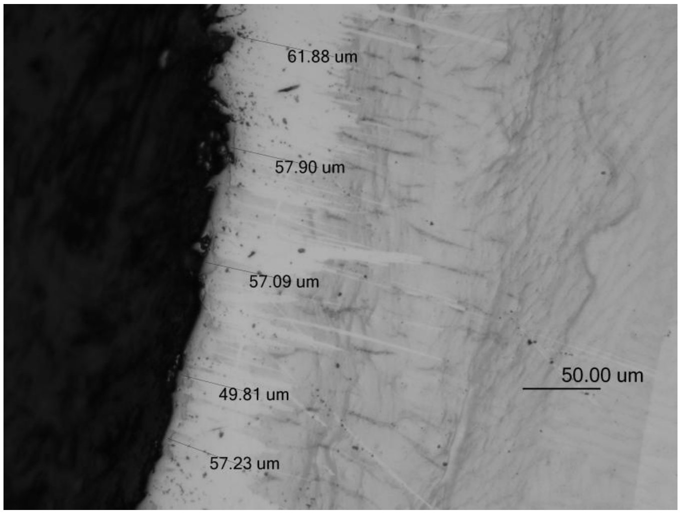

Figure 12: Optical view (20x) of a Ti-6-4 uncoated sample at 6 hrs & 1750°F

It can also be seen that the oxygen did not diffuse evenly or create a clean boundary between the alpha and alpha-beta phases. It is important to note this because it can have an effect on how much titanium must be milled off of each forging by WGC.

4.1.2 Phase Structure

The second difference we noted between alpha phase and alpha-beta phase was a difference in phase structure. For some samples of alpha case, as seen in Figure 13, the alpha case region had a different structure than the alpha-beta region.

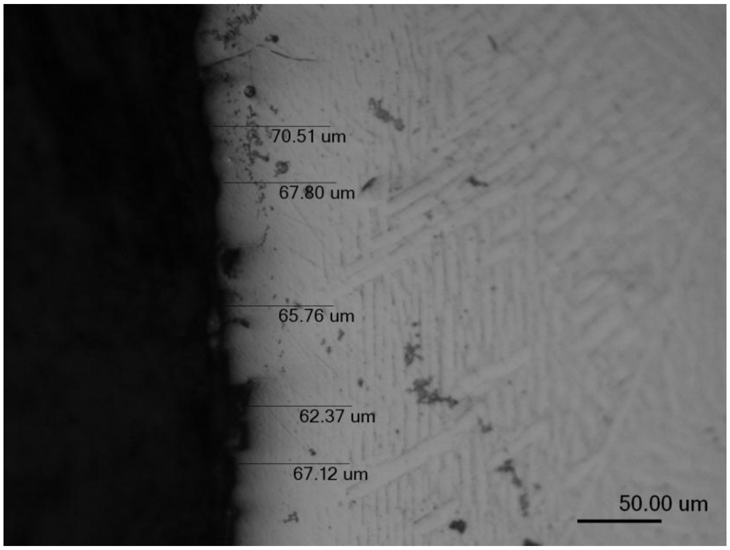

Figure 13: Optical view of a Ti-6-4 SJ coated sample at 6 hrs & 1750°F

The alpha case can be noted by a smooth and homogeneous appearance whereas the alpha-beta region has both regions of alpha and beta case dispersed within one another. Photos of each of the sample’s alpha case region and measurement can be found in Appendix H.

4.2 Alpha case depth trends

We viewed each sample beneath the optical microscope and took five measurements from the edge of the sample to the beginning of the alpha-beta region. The average of these five measurements determined the depth of alpha case region. Figure 14 shows the depth of the alpha case region for the Ti-6-4 samples, which we inferred from visual measurements.

4.2.1 Microscopic analysis

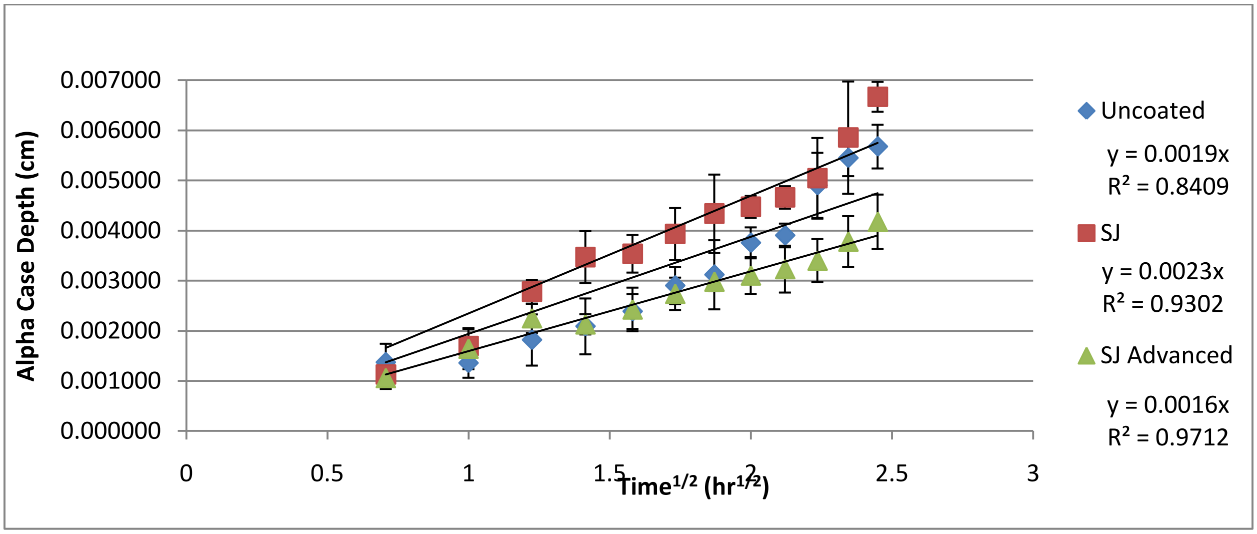

Figure 14: Diffusion Kinetics Ti-6-4

A parabolic rate was originally found when viewing alpha case as a function of time. This trend is consistent with expectation as a previous report by WGC showed a parabolic increase of alpha case over time until a point at which the alpha case depth reached a plateau and remained constant (Park, 1988). However, in order to represent these trends in a simpler, clearer, and linear fashion Figure 14 was plotted as alpha case depth as a function of the square root of time (Dannheim & Sisson). The positive slope of the line shows with increasing time there is an increase in growth. Alpha case depth is not only a function of the temperature but a function of the time exposed to the heat source. The trends also show that samples with SJ coating had the most alpha case whereas samples with SJ advanced had the least alpha case. The uncoated samples fell somewhere in the middle of the range.

The data which we compiled through our heating trials was compared to paper titled, *Alpha Case Layer Growth Kinetics for (α+β) Ti-6-4 from 732°C to 954°C* (Dannheim & Sisson), which also measured alpha case depth over time. Table 2 and

Table 3 compare the data which we gathered to the data reported in this paper.

Table 2: Comparison to Alpha Case Layer Growth Kinetics for Ti-6-4 by F. Dannheim and R.D. Sisson

Time (hrs)	Alpha Case Depth @1749.2 F (cm) (Dannheim & Sisson)	Alpha Case Depth @ 1750 F (cm) (Chretien, King, Proia, Rudolf)
1	0.00777	0.001356
4	0.01023	0.003756

Table 3: Comparison to trend from Alpha Case Layer Growth Kinetics for Ti-6-4 by F. Dannheim and R.D. Sisson

Report Author	Trend line equation	R^2 value
(Dannheim & Sisson)	$Y = 0.0062XY$	0.8947
(Chretien, King, Proia, Rudolf)	$Y = 0.0019x$	0.8409

The data in Table 2 shows that when comparing the alpha case depth at similar points in time, Dannheim and Sisson suggest more growth per time. Referring to

Table 3 also shows that the slope calculated in our analysis is 1/3 of their reported slope. Although our trend line's R^2 value is 0.8409, we have collected 12 points where as the report by Dannheim and Sisson collected only 3 points. When a figure only has 3 points, any change in the depth of alpha case can significantly change the slope. Therefore although our data does not exactly match up to the paper by Dannheim and Sisson, there is not enough data to statistically say which one is accurate.

The data for optically measured depth of alpha case for ELI is plotted in Figure 15 as depth as a function of square root of time.

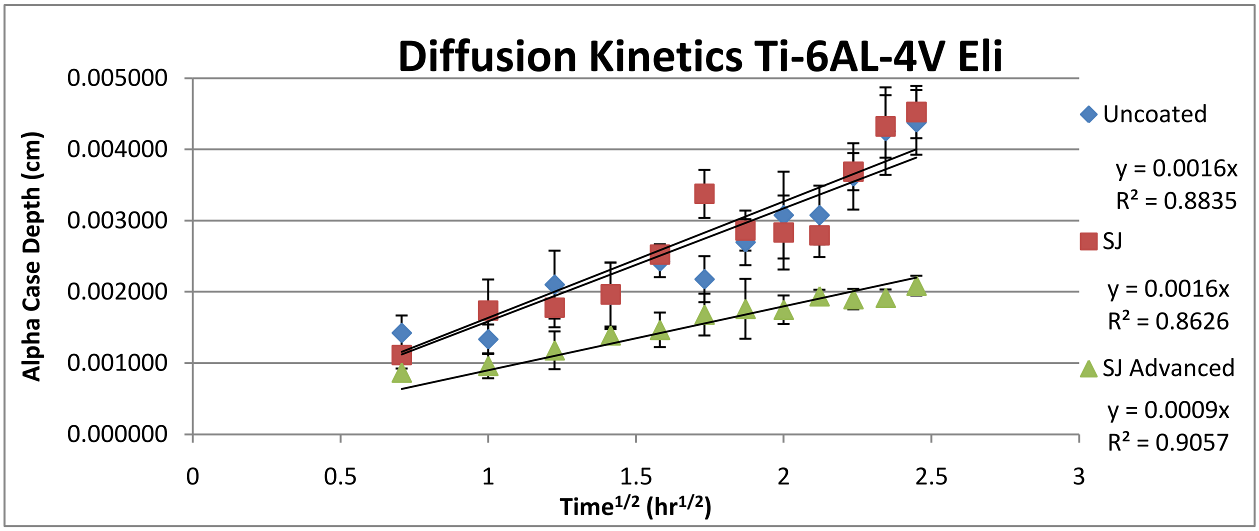

Figure 15: Diffusion Kinetics ELI

The data for all trials of ELI show the similar relationships to the data for Ti-6-4. The linear trend lines show that there is a positive growth trend between the depth of alpha case and square root of time. Again, with these axis conditions a linear trend represents an actual parabolic growth rate. The various coatings are also ranked in the same order as with Ti-6-4. The SJ coated showed the most alpha case where as the SJ advance coated showed the least alpha case. The use of SJ advanced coating reduced the alpha case formation by about 50%. All data used in optical depth analysis can be found in Appendix I.

4.2.2 Microhardness analysis

In addition to microscopy, we recorded microhardness profiles to determine the actual depth of the alpha layer diffused into the titanium. Since the alpha case surface is much harder than the titanium itself, it is necessary to determine the depth at which the surface hardness stabilizes, as shown in Figure 16.

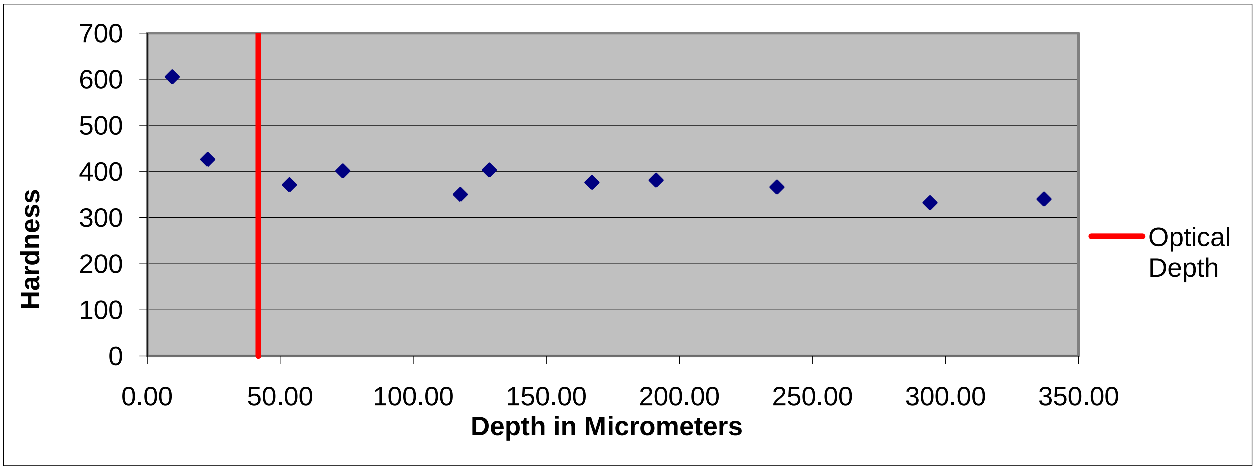

Figure 16: Micro-hardness data Ti-6-4 SJ advanced coating at 1750°F

As can be seen in Figure 16, the micro-hardness testing for the SJ advanced coating shows an alpha case region all the way to 50 micrometers. Whereas the optical measurement reflects that the alpha case region ends at 42 micrometers. This occurs as the alpha phase diffuses into the beta region creating a harder and unwanted alpha-beta phase. The alpha case depth using microhardness testing shows a 120% increase compared to optical analysis. The rest of the values for microhardness testing were compared to optical data in Table 4.

Table 4: Alpha case depth comparison of optical microscopy and microhardness at 6 hr and 1750°F

Titanium Grade	Coating Condition	Optical Depth (μm)	Microhardness Depth (μm)	Microhardness to Optical Increase
Ti-6-4	Uncoated	57	90	60%
Ti-6-4	SJ	67	110	60%
Ti-6-4	SJ advanced	42	50	20%
ELI	Uncoated	43	80	90%
ELI	SJ	45	100	120%
ELI	SJ advanced	21	30	40%

By using the estimated values for where microhardness testing stabilizes, we determined how far beyond the optical data the alpha phase actually goes. These values range from 120% to 220%. These values should be kept in mind when determining how much alpha case to mill off after heating. Microhardness profiles and measurements for each category of sample can be found in Appendix J while the data can be found in Appendix K.

4.3 Cost analysis

In order to determine economic viability of changing the industrial forging process from their current SJ coating to the proposed SJ advanced coating and optimizing the milling process, a cost analysis was performed. The cost analysis takes into account only the raw materials: acids and coatings. Since our previous findings have shown a reduction in alpha case through SJ advanced coated samples, it must be determined whether this reduction correlates to a large enough reduction in the amount of acid needed to make the process more economical. The cost analysis does not take into account savings on acid disposal, labor cost, or increased production time, or even distinguish between Ti-6-4 and ELI. It simply takes into account the worst case scenario to estimate potential savings. Actual savings, therefore, are expected to be even larger.

4.3.1 Acid Bath

Currently, WGC mills 0.015 inches off each titanium piece regardless of time heat-treated of titanium grade. From optical microscopy, we found the largest depth of alpha case to go only 0.0026 inches into the surface based on current process conditions. By adding a safety factor of a 120% increase, the largest depth beyond microscopy in which the microhardness profile stabilized, we determined the final depth of alpha case that should be removed is 0.0057 inches, as shown in Table 5. Therefore, there is a significant opportunity to optimize the milling process. Similarly, the SJ advanced coating showed an even greater reduction in alpha case formation. A transition to this coating would reduce the amount of milling currently performed by about a factor of 4.

Table 5: Milling Adjustments

	Current Process	Optimized Milling	SJ Advanced Coating
Max Depth @ 6 hrs (in)	0.0026	0.0026	0.0017
120% Safety Factor (in)		0.0031	0.0020
Amount Milled (in)	0.0150	0.0057	0.0037
Reduction Ratio		2.6	4.1

This reduction in chemical milling would increase the current bath life of approximately 14 days to 36 days if milled more efficiently or to 56 days by using the SJ advanced coating. Therefore the number of acid baths a year could be reduced from 26 down to 7, as shown in Table 6. Based upon this reduction in acid baths per year and the purchasing and pricing information received from WGC for 2009, a savings of over $400,000 is possible for simply milling the titanium more accurately, and a potential of just over $500,000 could occur through utilizing the SJ advanced coating as the raw material cost of the acid baths is significantly reduced.

Table 6: Acid Bath Cost Analysis

	Current Process	Optimized Milling	SJ Advanced Coating
Acid Bath Life (days)	14	36	56
Baths (per yr)	26	10	7
Amount HF in 2009 (lbs/yr)	445,000	179,000	111,000
Amount HNO3 in 2009 (lbs/yr)	350,000	136,000	88,000
Cost HF ($/lb)	$1.39	$1.39	$1.39
Cost HNO3 ($/lb)	$0.21	$0.21	$0.21
Total Acid Bath Cost ($/yr)	$688,000	$267,000	$172,000
Savings ($/yr)		**$421,000**	**$516,000**

4.3.1 Coatings

Based on the total amount of SJ coating purchased by WGC in 2009 and the price difference between the SJ and SJ advanced coating, a comparison between the net purchasing price for each coating is shown in Table 7. Since the SJ advanced coating is $2.25 more expensive the total cost of coat will be approximately $4,800 more expensive annually.

Table 7: Coating Cost Analysis

	Current Process	Optimized Milling	SJ Advanced Coating
Coating Cost ($/gal)	$19.75	$19.75	$22.00
Total Gal (2009)	2150	2150	2150
Coating Cost ($/yr)	$42,500	$42,500	$47,300
Added Cost ($/yr)		**$0**	**$4,800**

4.3.2 Overall

Finally, by combining price comparisons of both coating and acid bath cost for all three processes, as shown in Table 8, a potential savings of over $400,000 is determined for simply optimizing the current milling process and a project savings of just over $500,000 is possible by using the SJ advanced coating.

Table 8: Overall Cost Findings

	Current Process	Optimized Milling	Proposed SJ Adv. Coating
Coating Cost ($/yr)	$42,500	$42,500	$47,300
Acid Bath Cost ($/yr)	$688,000	$267,000	$172,000
Total Coating and Acid Cost ($/yr)	$731,000	$310,000	$219,000
Savings ($/yr)		**$421,000**	**$512,000**

4.4 Environmental Benefits

Another important factor that should not be overlooked is the environmental benefit as a result of optimizing the milling process. Nitric and hydrofluoric acid are extremely dangerous and pose a potential risk to the environment if not disposed of properly. Therefore, any reduction in the quantities purchased will reduce the risk of an acid spill, as occurred in 1993 (Leonhardt, 1993), and the necessity for a third party vendor to remove and treat the waste.

4.5 Coating comparison

The current coating used at the WGC, SJ, has mica and sodium silicate in it. The SJ advanced coating tested contains glass frit and alumina. Thus, the new coating is ceramic based and forms a thicker layer over the pieces. The melting point of the SJ coating is 2000°F, while the melting point of the SJ advanced is 1700°F. Because the furnaces are heated to 1750°F, a potential problem would be the coating melting and getting into the machines.

4.6 Vacuum Testing

Upon etching the vacuum tested sample with the Kroll's reagent of hydrofluoric and nitric acid, a clear distinction can be seen in the microstructure of the alpha case as opposed to the alpha-beta phase, as shown in Figure 17.

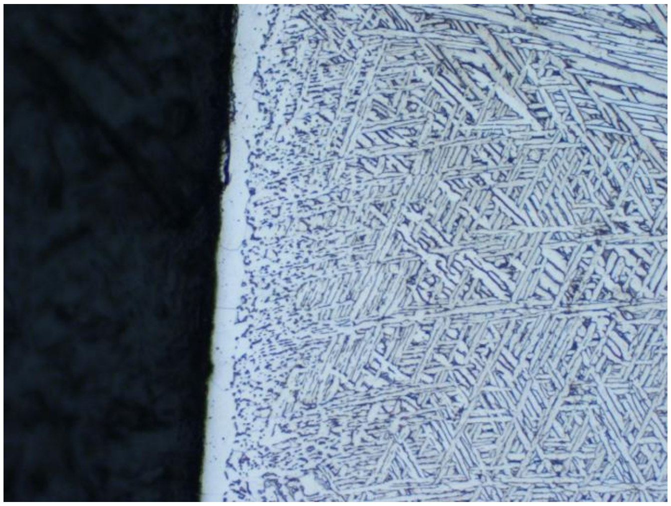

Figure 17: Uncoated Ti-6-4 vacuum heated sample

The alpha case is clearly seen as the solid white section with a depth of approximately 12 microns. Therefore, a reduction of about 80% is achieved during heat-treatment under vacuum conditions, as shown in Table 9.

Table 9: Vacuum Sample Comparison

Sample Condition	Grade	Time	Temperature	Depth of Alpha Case
Atmospheric	Ti-6-4	6 hours	1750°F	57
Vacuum	Ti-6-4	6 hours	1750°F	12

4.7 Limitations to findings

The following sections describe those parts of our project that may have accrued some error in measurements while testing or those areas in which further investigation should occur.

4.7.1 Application method

Although we applied the coating to the titanium specimens for both the SJ and SJ advanced coating trials, we cannot fully ensure that the method of coating application effectively covered the sample. For both trials the twelve specimens were dipped into large containers of coating at Wyman-Gordon. This application method could have cause abnormalities in coating thickness. The coating solution may not have been evenly dispersed within the containers and therefore only the least dense solution may have coated our samples. Additionally by dipping a sample into the container, the coating streaked and may have caused an uneven layer of coating across the sample. These abnormalities in coating thickness may skew our data to show a coating was less effective than it actually is.

4.7.2 Furnace trays

The furnace trays may have caused abnormalities in our alpha case depth measurements. Each specimen was placed on a furnace tray where two sides were in contact with a metal tray and the others were directly exposed to the atmosphere inside the furnace. The diffusion kinetics of oxygen into titanium may have been hampered by the tray as oxygen was more plentiful on those sides exposed to the atmosphere as opposed to the sides in direct contact with the tray.

4.7.3 Coating durability

Our data only shows trends for alpha case prevention during the initial heating cycle of the metal forging process. Several other operations take place at high temperatures where alpha case can form including forging and reheat. The coating was not evaluated to see if it could withstand the cooling and reheat cycles as well as the compression forces of forging while still maintaining a similar level of alpha case prevention. Additionally, the SJ advanced coating was not tested to determine if it had the lubrication properties necessary for metal movement inside of a forge die. These additional tests were outside the scope of our project but should be conducted before any coating transition could occur.

4.7.4 Coating viability and removal

A final limitation which was outside the scope of our project was to test the samples to determine if any of the coatings had diffused into the titanium or how the coating may have affected the final properties of the titanium. Additionally, the coating formed a hard crust layer over the metal once it was removed from the oven. We did not investigate how to remove this layer from the specimens. However, the supplier, Advanced Technical Products, recommended sandblasting or chemical etching as a method of removal.

5 Conclusions

The intent of the project was to develop a profile for the buildup of alpha case on Ti-6-4 and ELI, determine if coatings could be used to reduce or eliminate the alpha case on these samples, and conduct a cost analysis to determine if changing the coating would be economically viable. This section outlines several conclusions which we reached based on our research.

The SJ coating, currently used by Wyman-Gordon, did not reduce the alpha case layer thickness on the samples. The general trend for the SJ coating trial showed the largest build up of alpha case out of all heating trials. At some points in time, the alpha case layer was equal for the uncoated sample and the sample coated with the SJ coating. The ELI samples did not show a significant difference in the alpha case layer between the SJ coated and uncoated samples. Therefore the coating currently used at WGC does not aid in alpha case prevention.

The SJ advanced coating significantly reduced the alpha case on both the Ti-6-4 and ELI samples. Samples with the SJ advanced coating had a consistently smaller amount of alpha case on the outer edge of the surface. The Ti-6-4 sample with the advanced coating had about a third less alpha case than the uncoated sample when heated for six hours, while the ELI sample with the advanced coating had only half as much alpha case as the uncoated sample after six hours. Thus, the advanced coating reduced the alpha case layer by a significant amount.

The WCG currently mills off more material than just the alpha case layer. The WCG currently mills 0.015 inches off every titanium piece regardless of how much alpha case is actually on the piece. Based on our microscopy and microhardness results, the alpha case depth is found a maximum at 0.006 inches for their current conditions. Therefore, WCG is using is not milling efficiently and can begin to save over $400,000 annually by optimizing their milling process. This monetary savings is in addition to the environmental benefits of reducing the total amount of acid the company needs to store and eventually have treated. Any reduction in the quantity of acid purchased lowers the risk of a potential spill.

Based on the cost analysis, it is in the economic interests of the company to switch to the SJ advanced coating. Although the SJ advanced coating is slightly more expensive, it reduced the amount of alpha case on the titanium pieces by a factor of four. Since much less alpha case would be necessary to remove, the acid baths would last much long. Based upon our cost analysis of both coatings and acid baths, the SJ advanced coating shows a potential savings of just over $500,000 and therefore should be utilized by the WGC.

6 Recommendations

Based upon the conclusions discussed above, we have developed a set of recommendations for further research on the use of coatings to prevent or minimize alpha case formation.

We recommend WGC optimize their milling process and determine an adequate safety factor. From our results it is clear that WGC mills much more titanium from each piece than is necessary to completely remove the alpha case layer. Our project showed a more accurate measurement of how deep the alpha phase actually diffuses into the titanium. The safety factor we assumed was simplified to the largest percentage increase between microscopy depth and microhardness profiles. However, more detailed testing would need to be performed to determine a more accurate safety factor to account for when milling samples. However, a potential for large savings of over $400,000 is possible if the milling process is used more efficiently to remove only the alpha case layer and a given safety factor.

Upon further testing, the WGC should begin using the SJ advanced coating. The cost analysis shows a significant potential for savings if the SJ advanced coating is introduced to the process. The coating showed a significant improvement in alpha case prevention when compared to the uncoated titanium and the current SJ coating. However, more tests need to be done to make sure that more alpha case does not form through the reheating and forging process, and also that the coating is capable to be used on the equipment. Potentially, a switch to the SJ advanced coating could save WGC over $500,000 annually.

We recommend that titanium samples be heated over a longer time scale to get a full profile of alpha case buildup until the alpha case layer ceases to grow. At some point, the alpha case layer profile over time will reach a plateau. Our recommendation is to heat samples of both types of titanium to determine the maximum depth of alpha case build up over time. This testing can be done with both coatings as well as uncoated samples. WGC may be able to further refine their milling process by knowing the maximum depth of alpha case on titanium products.

We recommend that titanium samples are tested simulating each process step that titanium parts undergo including being spray coated, hydraulically pressed, and recoated. At WGC, the coatings are sprayed on. However, in our testing the samples were dipped in the coating, which could result in a different thickness of coating and therefore alpha case depth. If the coating layer were thinner, it may not prevent alpha case as well. Further, the titanium at WGC is forged and reheated. The coating may not mold with the titanium, which could lead to cracks or holes in the coating layer. These inconsistencies in the coating layer could allow oxygen to diffuse in and create more alpha case. Another possible challenge could be that the coating may stick to the hydraulic press. Tests should be completed to ensure that the coating will prevent alpha case throughout the entire process without damaging the equipment.

More tests should be completed to determine the extent of the interaction between the SJ advanced coating and titanium samples. Because titanium is extremely reactive, some of the components from the coating could diffuse into the alpha case. Tests should be done with x-ray diffraction to test the surface of the titanium to determine the elements in the sample and the phase of titanium at various depths.

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current&date=Aug+5,+1993&author=Leonhardt,+David&pub=Boston+Globe&edition=&startpage=46&desc=Acid+spill+angers+North+Grafton+residents

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Appendix A – Equipment used in testing and analysis

A.1 Electric Oven (5217) and P.P.E.

A Lindenberg electric furnace located in the heat-treatment area of WGC was used to test titanium samples under conditions to form alpha case. This electric oven was chosen due to the fact that both gas fired and electric furnaces exhibit the same rate of alpha case build according to a WGC R&D report titled “Alpha Case and Hydrogen Absorption of Thin Section TI Forgings” (Park, 1988). It was beneficial because of the added advantage that the utilization of electric furnace 5217 did not inhibit production to the same extent which using the gas furnace would. Personal Protective Equipment (P.P.E.) was worn while introducing or removing titanium samples from the furnace. The P.P.E. included: face shield, lab glasses with side shields, thermally insulated gloves and thermally insulated jackets.

A.2 Saw in Washburn

A Mark V Series 600 saw in Washburn shops at Worcester Polytechnic Institute was used in order to cut samples to a size in which the buildup of alpha case could be examined beneath a microscope and micro hardness testing instrument. The saw used an S/C 6 x 0.040 x 5/8 blade which was rated for use with titanium alloys.

A.3 Vibro-peen

In order to maintain traceability within the samples collected a vibro-peen was used to grind the appropriate label, as described in Appendix B, on both the heat-treated titanium piece as well as the top of the mounted sample.

A.4 Coater

Samples were hand coated with SJ advanced coating by dipping them into the coating and being allowed to air-dry. Samples being coated with the SJ coating currently used at WGC were sprayed on and allowed to air-dry.

A.5 Sample Mounter

A Buehler SimpiMet® 3000 Automatic Mounting Press was used to encase our samples and create a mount suitable for optical and micro-hardness testing. The mounting cycle occurred at

4200psi and consisted of a 6 minute preheat to 300°F, 2 minutes of heating, and a 3 minute cool period. A Buehler Phenolic Powder was used as the filler to encase the sample.

A.6 Grinding

The polisher used was a Buehler MetaServ 2000 grinder/polisher. The samples were polished by a manual method in which the mounted sample was pressed against the rotating wheel. Sandpaper grade 180-, 320-, and then 600-grit respectively to remove scratches from sample piece. Next a fabric polisher was used with a 1.0 and then 0.05 micron alumina solution to polish samples to a scratch free, mirror-like quality.

A.7 Optical Microscope

To view the depth of alpha case within each sample a Nikon Epiphot microscope was used at 20 times magnification. The ACT-2U computer program was utilized in conjunction to measure the alpha case depth and capture pictures of each sample.

A.8 Micro-hardness Tester

To obtain a more accurate measurement of the alpha case and to estimate the error in our visual readings, microhardness testing was performed using the Shimadru HV-2000 Microhardness Tester. To use, samples were placed in the microscope, and measurements were made using the Vickers Microhardness scale.

Appendix B – Traceability and labeling technique

The samples were labeled with a marker after they were removed from the oven and with a vibro-peen on the remaining sample once they are cut.

1. Collect 12 samples each kind of titanium alloy. The first digit represents the grade.
   a. Ti 6-4 (A)
   b. Ti 6-4 Eli (B)
2. The second character in the identification code defines what type of coating, if any, that the sample has on it.
   a. Uncoated (X)
   b. ATP - Sodium Silicate coating (Y)
   c. ATP - Sodium Silicate advanced coating (Z)
3. Place the 12 samples of the same grade, coating, and coating classification on an oven tray in an organized order.
4. When removing the samples from the furnace place samples in chronological order of when they were removed for traceability.
5. The third character is labeled as 1 through 12 to represent the order in which the sample was removed from the oven and the length of time that the sample was inside the furnace.

A full identification number includes: Grade, coating classification, sample #

Appendix C – Heating Procedure

1. Heat electric furnace 5217 to temperature depending on temperature for the specified grade.
    a. Ti-6-4 1750 ^{0} F
    b. ELI 1750 ^{0} F
2. Adjust the temperature on the control panel to the rear and right side of the oven
    a. Set temperature should be the temperature which the specific grade calls for
    b. Control temperature should be no more than 100 ^{0} F more than the set temperature.
3. Remove the samples in 30 minute increments over a period of 6 hours
4. Two people are needed to remove a sample from the electric furnace
5. The person (person 1) who will be removing the sample from the oven should put on P.P.E. including a thermally insulated jacket, thermally insulated gloves, face shield, and lab safety glasses with side shields.
6. The other person (person 2) who will be removing the sample from the tray should put on a thermally insulated gloves, face shield, and lab safety glasses with side shields.
7. Person 2 should open the furnace by using the foot pedal to the left of the furnace
8. Person 1 grabs the furnace tray from inside the furnace with a pair of industrial tongs
9. Person 2 removes the hot sample from the furnace tray with a pair of industrial tongs and sets it down on a cold furnace tray on the table adjacent to the furnace
10. Once the sample is removed, it should be left to cool for 24 hours.

Appendix D – Cutting Procedure

D.1 Procedure in the Test Prep Department of WGC

Made arrangements with Ernie Brackett in the Test Prep department at WGC for employees to use an industrial saw that would cut through samples with alpha case build up in a timely fashion. The operators cut the sample in two directions before returning the labeled samples to our team.

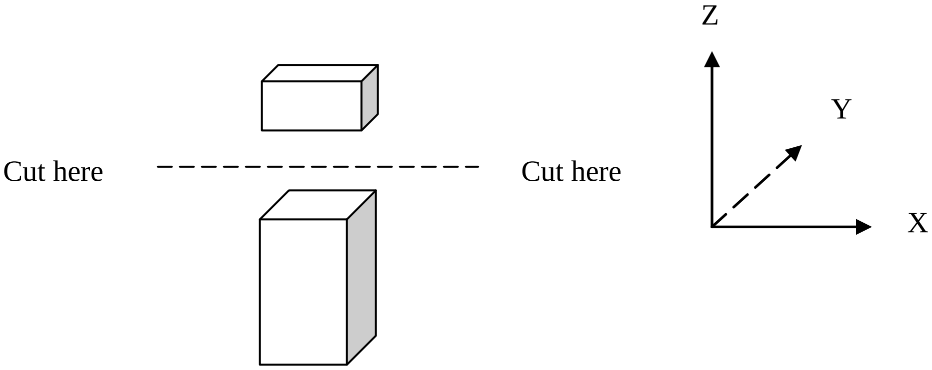


Figure 18: First cut at WGC

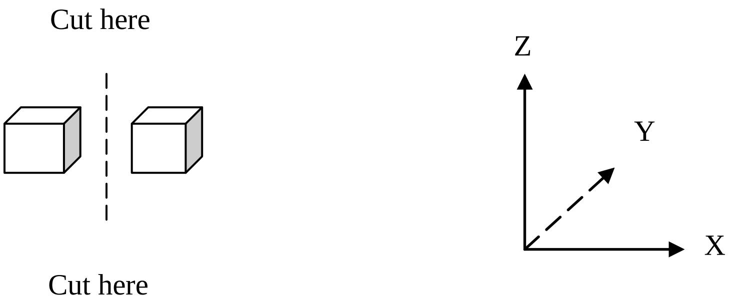


Figure 19: Second cut at WGC

D.2 Procedure in Worcester Polytechnic Institute’s Materials Lab

To prepare each sample for analysis the final ½ inch of the sample was removed in the xy-planar direction to expose alpha case.

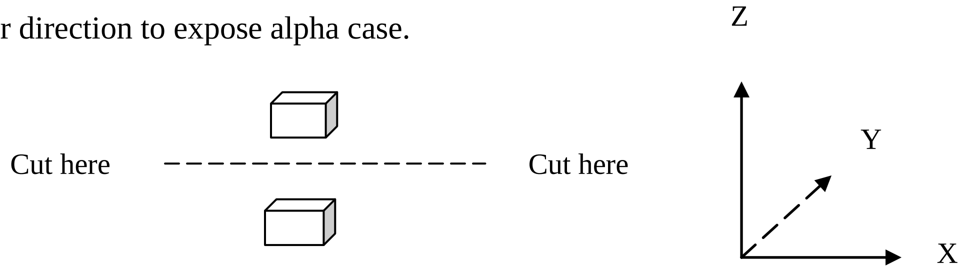


Figure 20: Final Cut

1. Create 1 to 10 coolant solution by measuring coolant and water out in a graduated cylinder
2. Pour coolant solution into the cooling water reservoir on the Mark V Series 600 saw
3. Place S/C 6 x 0.040 x 5/8 grade saw blade on to the Mark V Series 600 saw and tighten bolt with a wrench
4. Place sample into the sample holder as depicted in Figure 3 and close the safety shield on the saw
5. Turn on saw by pressing the start button located on the front panel
6. Lower the sample on to the saw blade which is already in motion
7. Continue to check on sample until it is cut entirely through
8. Turn off saw and repeat for remaining samples

Appendix E – Sample Preparation Procedure

E.1 Mounting

In order to perform the necessary testing on each titanium sample they must first be mounted by the following procedure.

1. Turn on Buehler SimpliMet® 3000 Automatic Mounting Press by pushing the *power* button.
2. Insert sample piece face down and centered on stage with the side which will later be viewed during testing. Lower stage
3. Measure 20-25cc of Buehler Phenolic Powder and pour onto sample using a funnel.
4. If mounting two samples at once, insert spacer and repeat steps 2 and 3.
5. Secure cover and click the *cycle start* button.
6. Lower stage completely to reduce pressure then unfasten cover.
7. Raise stage to open cover and clean area of any leftover residue.

E.2 Polishing

After a sample is mounted it must be polished on the xy-plane in order to have a clean surface to look at under the microscope

1. Uncover the polishing surface on the Buehler MetaServ 2000 grinder/polisher.
2. Begin with 180-grit sandpaper as the polishing surface.
3. Open the water valves corresponding to the main line and the water nozzle above the grinding surface.
4. Engage the water flow then engage the polisher to spin.
5. Apply pressure to mounted sample in order to polish the titanium piece.
6. Rinse sample with water once polished.
7. When all samples are polished, repeat steps 2-6 using 320-grit sandpaper.
8. Repeat steps 2-6 again with 600 grit-sandpaper.
9. Next, start MicroPolisher II by turning power switch and moving switch to *start* position.
10. While polishing apply 1.0 micron alumina solution as needed.

11. Rinse each sample after finished polishing.
12. Repeat steps 9-11 using 0.05 micron solution station.
13. Thoroughly rinse polishing cloth then apply MasterMet colloidal silica polishing suspension.
14. Polish each sample for few seconds on the preceding solution then place in Buehler UltraMet 2002 Sonic Cleaner.
15. Use blow-dryer to dry each sample.

E.3 Etching

The last step in sample preparation is to etch with a nital ethcing solution to cause the alpha case layer to visually stand out from the rest of the titanium.

1. Pour 100 ml ethanol into 250 ml glass beaker.
2. Combine 3-5 ml nitric acid with ethanol.
3. Dip cotton swab into acid solution and wipe onto titanium sample for 10-15 second.
4. Rinse sample in water to stop etching.
5. Apply acetone to second cotton swab and wipe sample to clean.

Appendix F- Optical Microscopy Analysis Procedure

To determine the depth of alpha case the optical microscope was used by the following procedure.

1. Turn on microscope by increasing brightness to level between 9 and 10.
2. Open ACT-2U program on the computer desktop.
3. Place sample on stage and view edge of sample to search for alpha case location.
4. Upon locating alpha case take five measurement of depth via steps as described in step 5 and 6.
5. In ACT-2U program click “Tools” then “Length” then “point-to-point”.
6. Click the mouse on the edge of the sample and extend the line until alpha case ends. Click mouse again to view length.
7. Take picture of sample by labeling appropriately, then clicking “apply”, and then selecting “capture”.

Appendix G – Microhardness analysis Procedure

Using the Shimadru HV-2000 microhardness tester

1.) Set sample in the microscope
2.) Put oil on the diamond using a q-tip
3.) Focus the sample by adjusting the stage height
4.) Use the front and side adjustments to center the sample
5.) Zero the microscope
6.) Specify a load of 100 for 10 seconds
7.) Switch from the microscope to the diamond
8.) Press start
9.) Line the black lines with the edge of the diamond for a reading
10.) Rotate the lens 90^o and repeat step 9
11.) Press read and record values
12.) Repeat the procedure until the values are consistent, moving the diamond horizontally a half a diamond, and down at least 2-3 diamond lengths each trial

Appendix H – Alpha Case Optical Depth Photos

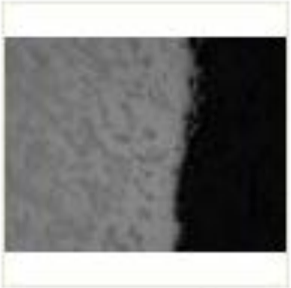

AX1Etch

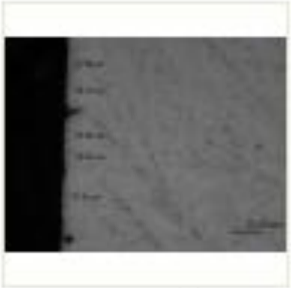

AX2Etch


AX3Etch


AX4Etch


AX5Etch


AX6Etch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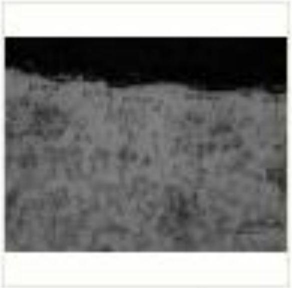
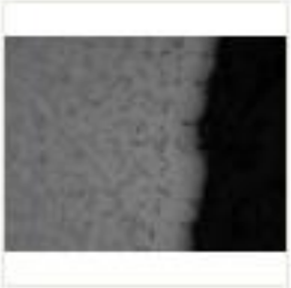

AX8Etch


AX9Etch


AX10Etch

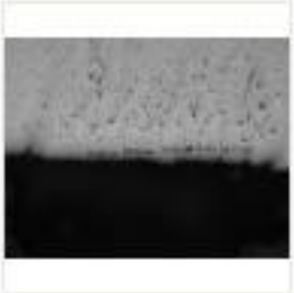

AX11Etch


AX12Etch


AY1Etch


AY2Etch


AY3Etch


AY4Etch


AY5Etch


AY6Etch


AY7Etch


AY8Etch


AY9Etch


AY10Etch


AY11Etch


AY12Etch


AZ1Etch


AZ2Etch


AZ3Etch


AZ4Etch

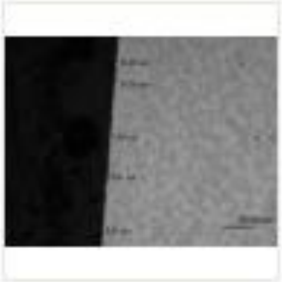

AZ5Etch


AZ6Etch


AZ7Etch


AZ8Etch


AZ9Etch


AZ10Etch


AZ11Etch


AZ12Etch


BX1Etch

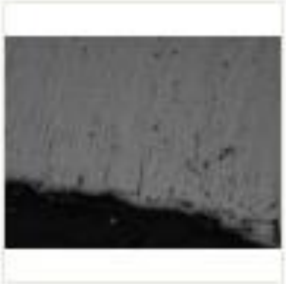

BX2Etch

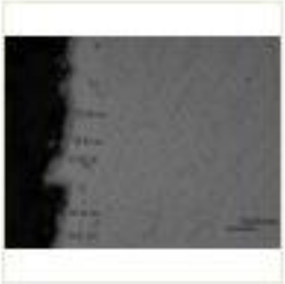

BX3Etch


BX4Etch


BX5Etch


BX6Etch


BX7Etch

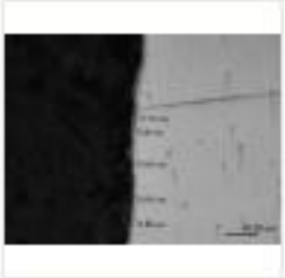

BX8Etch

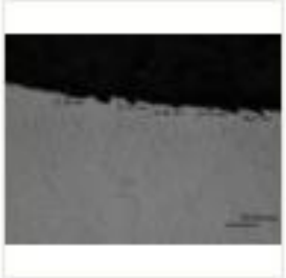

BX9Etch


BX10Etch


BX11Etch

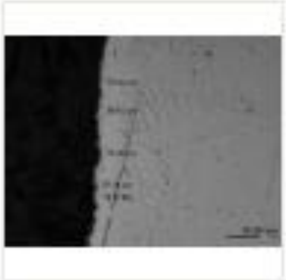

BX12Etch


BY1Etch


BY2Etch

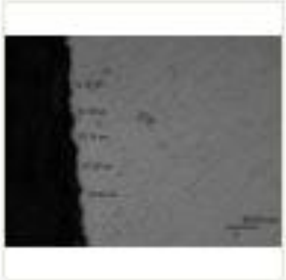

BY3Etch

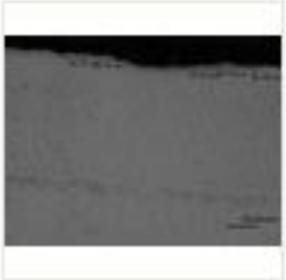

BY4Etch


BY5Etch


BY6Etch

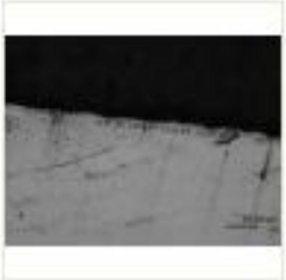

BY7Etch


BY8Etch


BY9Etch

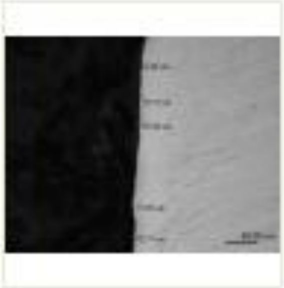

BY10Etch


BY11Etch


BY12Etch

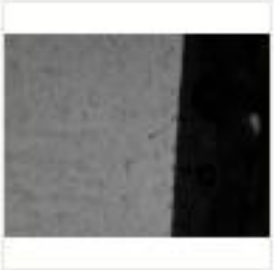

BZ1Etch


BZ2Etch

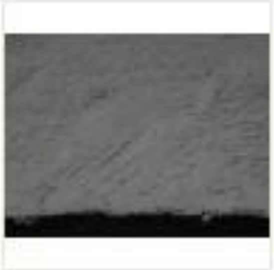

BZ3Etch


BZ4Etch

BZ5Etch



BZ6Etch



BZ7Etch

BZ8Etch

BZ9Etch

BZ10Etch

BZ11Etch

BZ12Etch

Appendix I – Alpha Case Optical Depth Data

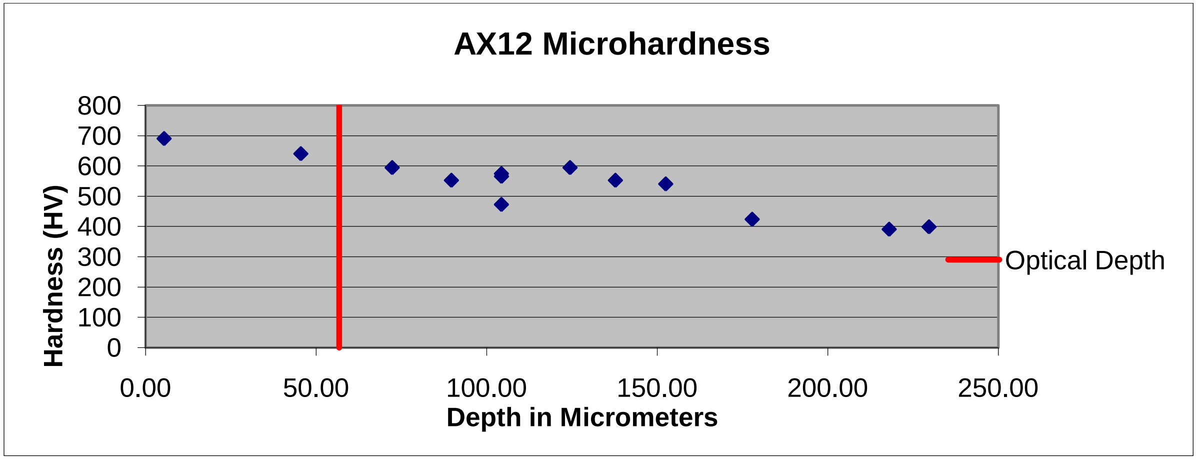
Sample	Measure 1 (μm)	Measure 2 (μm)	Measure 3 (μm)	Measure 4 (μm)	Measure 5 (μm)	Avg (μm)	Avg (cm)	Std Dev (μm)	Std Dev (cm)
AX1	12.20	17.64	17.63	9.49	11.53	13.70	0.0014	3.73	0.0004
AX2	17.63	14.92	11.53	13.56	10.17	13.56	0.0014	2.92	0.0003
AX3	21.03	13.56	25.76	14.92	15.59	18.17	0.0018	5.11	0.0005
AX4	18.31	25.77	27.80	14.92	17.64	20.89	0.0021	5.58	0.0006
AX5	22.37	22.37	21.02	23.73	29.83	23.86	0.0024	3.47	0.0003
AX6	28.48	25.76	25.76	30.51	34.58	29.02	0.0029	3.70	0.0004
AX7	21.02	29.16	35.26	39.32	31.19	31.19	0.0031	6.90	0.0007
AX8	35.26	39.33	34.58	42.03	36.62	37.56	0.0038	3.09	0.0003
AX9	35.93	38.64	40.68	42.00	37.97	39.04	0.0039	2.37	0.0002
AX10	50.17	50.63	44.75	58.37	41.36	49.06	0.0049	6.49	0.0006
AX11	48.81	54.92	57.63	57.63	53.56	54.51	0.0055	3.64	0.0004
AX12	61.88	57.90	57.09	49.81	57.23	56.78	0.0057	4.36	0.0004
AY1	9.52	10.26	14.25	10.17	12.20	11.28	0.0011	1.94	0.0002
AY2	12.20	17.63	15.59	21.69	17.63	16.95	0.0017	3.46	0.0003
AY3	25.76	27.13	26.44	31.86	27.80	27.80	0.0028	2.39	0.0002
AY4	35.93	27.80	32.54	35.25	42.01	34.71	0.0035	5.18	0.0005
AY5	33.90	36.61	41.36	33.22	31.87	35.39	0.0035	3.76	0.0004
AY6	35.93	31.86	43.39	42.04	43.40	39.32	0.0039	5.19	0.0005
AY7	34.58	37.97	41.36	51.53	51.53	43.39	0.0043	7.80	0.0008
AY8	47.46	45.43	41.36	44.75	44.75	44.75	0.0045	2.20	0.0002
AY9	45.42	45.42	49.77	48.14	44.40	46.63	0.0047	2.24	0.0002
AY10	62.39	46.11	51.53	40.68	51.53	50.45	0.0050	8.05	0.0008
AY11	73.23	65.09	58.98	43.39	52.21	58.58	0.0059	11.49	0.0011

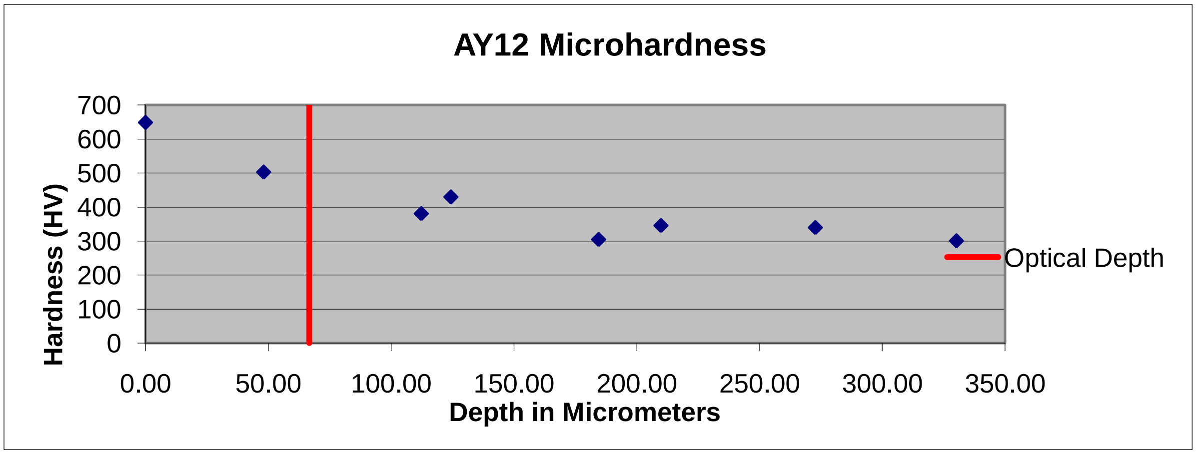
AY12	70.51	67.80	65.76	62.37	67.12	66.71	0.0067	2.98	0.0003
AZ1	8.81	12.20	9.49	13.56	8.84	10.58	0.0011	2.17	0.0002
AZ2	14.92	14.92	14.92	23.74	13.74	16.45	0.0016	4.11	0.0004
AZ3	27.12	21.69	22.37	19.00	22.38	22.51	0.0023	2.93	0.0003
AZ4	21.02	22.37	18.31	23.74	21.02	21.29	0.0021	2.01	0.0002
AZ5	21.69	18.98	24.41	25.76	30.52	24.27	0.0024	4.36	0.0004
AZ6	23.73	27.80	26.45	26.45	32.54	27.39	0.0027	3.23	0.0003
AZ7	31.19	27.80	31.86	30.51	27.80	29.83	0.0030	1.92	0.0002
AZ8	30.52	29.15	26.44	35.94	33.25	31.06	0.0031	3.67	0.0004
AZ9	27.15	27.33	35.28	35.26	36.62	32.33	0.0032	4.68	0.0005
AZ10	34.58	39.32	36.61	31.19	28.47	34.03	0.0034	4.30	0.0004
AZ11	40.68	30.52	34.58	42.03	41.36	37.83	0.0038	5.06	0.0005
AZ12	39.33	48.89	44.83	41.24	34.58	41.77	0.0042	5.43	0.0005

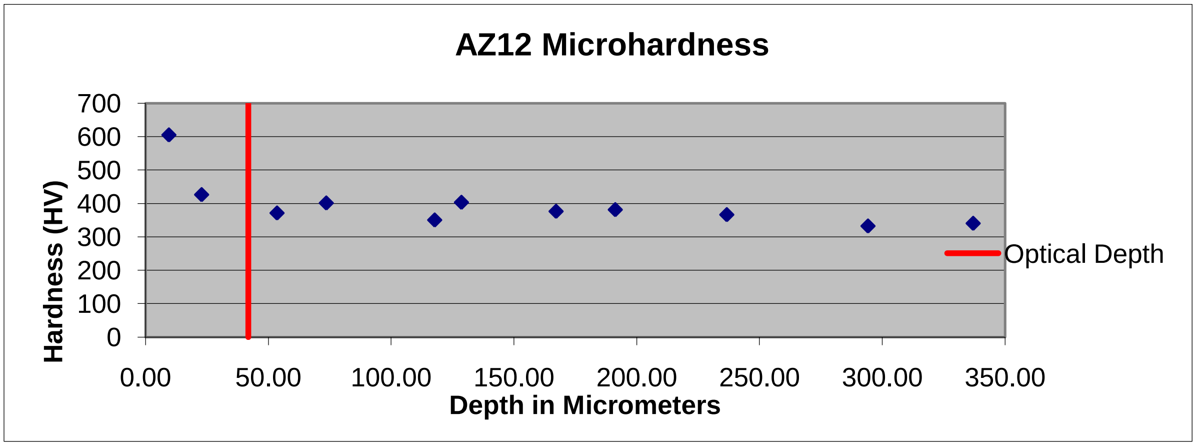
Sample	Measure 1 (µm)	Measure 2 (µm)	Measure 3 (µm)	Measure 4 (µm)	Measure 5 (µm)	Avg (µm)	Avg (cm)	Std Dev (µm)	Std Dev (cm)
BX1	14.92	10.85	14.24	17.63	13.58	14.24	0.0014	2.44	0.0002
BX2	11.53	13.56	11.53	16.58	13.56	13.35	0.0013	2.07	0.0002
BX3	20.35	18.31	20.34	29.15	16.95	21.02	0.0021	4.77	0.0005
BX4	24.44	20.34	23.05	13.56	16.27	19.53	0.0020	4.57	0.0005
BX5	22.41	27.12	21.69	25.09	25.12	24.29	0.0024	2.22	0.0002
BX6	24.41	17.07	19.85	24.41	23.19	21.79	0.0022	3.23	0.0003
BX7	29.83	29.15	26.44	21.69	27.80	26.98	0.0027	3.23	0.0003
BX8	27.80	38.65	33.23	22.38	31.87	30.79	0.0031	6.09	0.0006
BX9	27.12	35.93	33.90	26.44	30.52	30.78	0.0031	4.14	0.0004
BX10	30.54	42.72	33.90	38.67	35.26	36.22	0.0036	4.66	0.0005
BX11	42.71	47.46	38.65	34.58	49.49	42.58	0.0043	6.14	0.0006

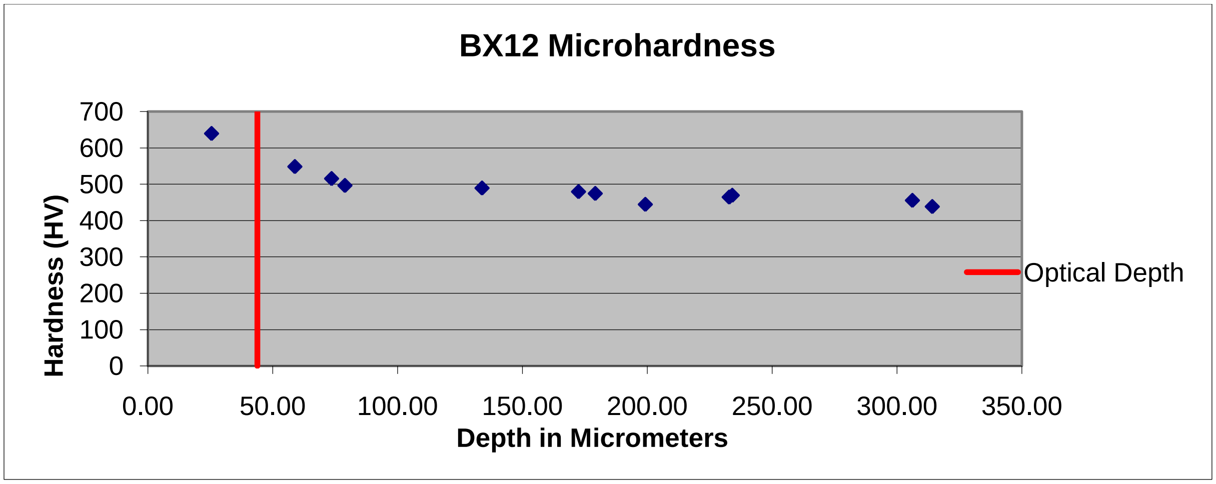
BX12	44.07	46.78	45.47	46.78	35.93	43.81	0.0044	4.54	0.0005
BY1	11.53	9.49	10.85	10.85	12.88	11.12	0.0011	1.23	0.0001
BY2	21.69	21.03	14.24	11.53	18.31	17.36	0.0017	4.38	0.0004
BY3	21.02	13.56	17.63	17.63	18.98	17.76	0.0018	2.73	0.0003
BY4	21.02	21.02	15.59	14.81	25.76	19.64	0.0020	4.50	0.0004
BY5	27.13	25.08	23.05	25.76	25.08	25.22	0.0025	1.47	0.0001
BY6	28.47	35.93	37.29	33.22	33.90	33.76	0.0034	3.37	0.0003
BY7	33.22	28.47	25.76	27.12	28.47	28.61	0.0029	2.81	0.0003
BY8	27.80	25.08	37.29	27.12	24.41	28.34	0.0028	5.20	0.0005
BY9	25.76	30.51	25.09	31.86	26.45	27.93	0.0028	3.04	0.0003
BY10	40.00	36.61	38.65	35.93	33.23	36.88	0.0037	2.61	0.0003
BY11	40.01	37.97	44.75	49.20	44.24	43.23	0.0043	4.39	0.0004
BY12	43.40	45.43	51.53	43.44	42.47	45.25	0.0045	3.67	0.0004
BZ1	9.49	8.81	8.14	8.14	8.81	8.68	0.0009	0.56	0.0001
BZ2	10.17	7.46	9.49	12.20	8.81	9.63	0.0010	1.75	0.0002
BZ3	9.49	10.17	15.59	13.59	10.17	11.80	0.0012	2.66	0.0003
BZ4	12.88	14.92	14.24	13.56	x	13.90	0.0014	0.88	0.0001
BZ5	11.53	12.95	14.93	16.96	17.00	14.67	0.0015	2.43	0.0002
BZ6	16.27	21.02	16.27	17.63	12.88	16.81	0.0017	2.93	0.0003
BZ7	14.24	18.98	15.59	24.41	14.92	17.63	0.0018	4.21	0.0004
BZ8	20.35	18.32	15.61	15.59	17.63	17.50	0.0018	2.00	0.0002
BZ9	18.31	18.98	20.34	18.98	20.35	19.39	0.0019	0.91	0.0001
BZ10	18.31	16.95	20.34	19.00	20.34	18.99	0.0019	1.44	0.0001
BZ11	20.34	19.98	18.31	17.63	19.66	19.18	0.0019	1.16	0.0001
BZ12	19.66	19.66	22.37	22.37	20.34	20.88	0.0021	1.39	0.0001

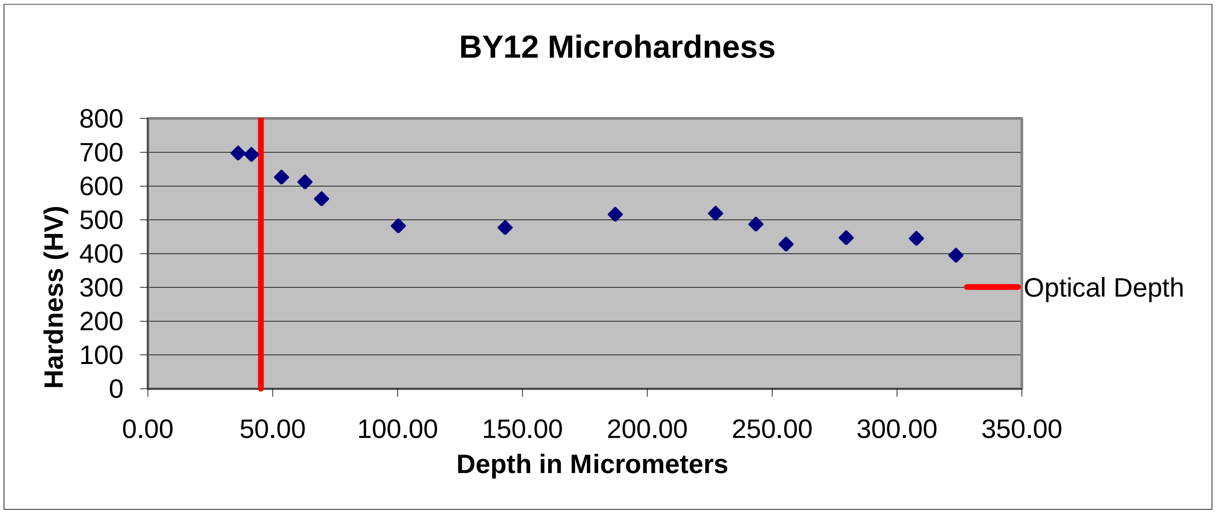
Appendix J – Microhardness Profiles

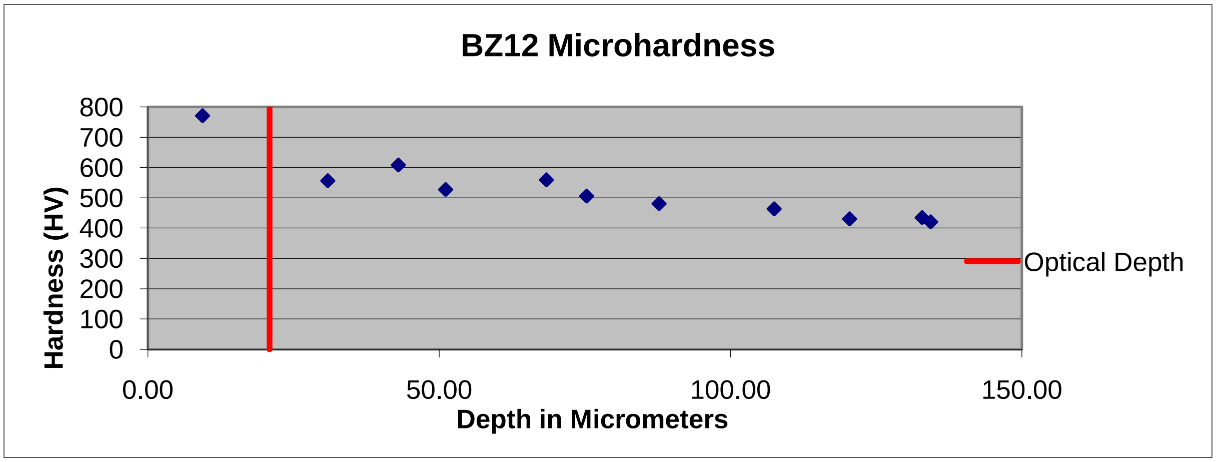







BX12 Microhardness
Hardness (HV)
700
600
500
400
300
200
100
0
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
Depth in Micrometers
Optical Depth


BY12 Microhardness
Hardness (HV)
800
700
600
500
400
300
200
100
0
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
Depth in Micrometers
Optical Depth


BZ12 Microhardness
Hardness (HV)
800
700
600
500
400
300
200
100
0
0.00
50.00
100.00
150.00
Depth in Micrometers
Optical Depth

Appendix K – Microhardness Data

	d1 (mm)	d2 (mm)	Hardness (HV)	Depth (µm)
For AX12				
1	17.2	18.2	691	5.35
2	16.6	17.4	641	45.45
3	17.7	17.6	595	72.24
4	18.1	18.5	553	89.61
5	19.6	20.0	473	104.28
6	18.0	17.3	595	124.40
7	18.4	17.8	566	104.29
8	17.9	18.0	575	104.28
9	18.8	18.2	541	152.46
10	17.4	19.2	553	137.70
11	20.6	21.2	424	177.81
12	22.1	21.4	391	217.99
13	22.5	20.6	399	229.67
For AY12				
1	17.4	16.4	649	0.00
2	22.9	21.2	381	112.30
3	22.6	26.7	305	184.51
4	24.7	22.0	340	272.76

5	26.0	23.6	301	330.22
6	19.2	19.2	503	48.13
7	20.2	21.3	430	124.36
8	22.7	23.6	346	209.90
For AZ12				
1	16.9	18.1	605	9.45
2	22.0	22.7	371	53.48
3	22.9	23.1	350	117.68
4	22.9	21.5	376	167.11
5	21.6	20.1	426	22.77
6	21.2	21.8	401	73.54
7	20.4	22.5	403	128.57
8	21.9	22.2	381	191.22
9	22.0	23.0	366	236.63
10	24.3	22.9	332	294.13
11	22.7	24.0	340	336.96
	d1	d2	HV	depth
For BX12				
1	17.0	17.0	640	25.44
2	20.6	20.0	549	58.82
3	18.7	19.2	516	73.53
4	19.2	19.4	497	78.88

5	19.4	19.5	490	133.80
6	19.3	20.0	480	172.46
7	19.7	19.8	475	179.16
8	20.6	20.2	445	199.22
9	20.3	19.4	470	234.05
10	20.4	19.5	465	232.81
11	20.4	19.9	456	306.22
12	20.7	20.4	439	314.18
For BY12				
1	17.6	16.8	626	53.48
2	16.3	16.3	697	36.10
3	16.1	16.6	693	41.44
4	16.8	18.0	612	62.89
5	17.7	18.6	562	69.52
6	18.7	19.5	482	100.27
7	19.9	19.5	477	143.05
8	19.3	18.6	516	187.17
9	19.0	18.8	519	227.34
10	19.4	19.6	487	243.50
11	21.0	20.6	428	255.57
12	20.7	20.4	447	279.67
13	20.4	20.4	445	307.78

14	21.6	21.7	395	323.63
For BZ12				
1	14.5	16.5	771	9.36
2	18.1	18.4	556	30.86
3	17.6	17.3	608	42.97
4	19.1	18.4	527	51.08
5	18.2	18.2	559	68.39
6	19.0	19.3	505	75.29
7	19.9	19.8	480	87.73
8	21.3	19.6	463	107.49
9	22.0	21.2	430	120.44
10	21.2	20.1	434	132.90
11	21.1	20.9	420	134.36